Mechanistic studies of the ethylene trimerization reaction with chromium – diphosphine catalysts: experimental evidence for a mechanism involving metallacyclic intermediates

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Supporting Information

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S1. Experimental Section

General Considerations

All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl, calcium hydride, or by the method of Grubbs.[1] Compound **1** and $CrPh_3(THF)_3$ were prepared as described previously.[2,3] Dichloromethane-d_2 was purchased from Cambridge Isotopes and distilled from calcium hydride. Other materials were used as received. Methylaluminumoxane was purchased from Aldrich. UV-Vis measurements were taken on a Hewlett-Packard 8452A diode array spectrometer using a quartz crystal cell. Elemental Analyses were performed by Desert Analytics, Tucson, AZ and by Midwest Microlab, Indianapolis, IN. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 300, or Varian INOVA-500 spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to internal solvent: 5.32 ppm, and 54.00 (t) ppm (CD_2Cl_2) for ^{1}H and ^{13}C data. ^{2}H NMR spectra were recorded on a Varian INOVA-500 spectrometer; the chemical shifts are reported with respect to an external D_2O reference (4.8 ppm).

Synthesis of $(PNP^{OMe})CrCl_3$ (2)

A dichloromethane solution (20 mL) of $CrCl_3(THF)_3$ (1.513 g, 2.9 mmol, 1 equiv) was added to a solution of **1** (1.098 g, 2.9 mmol, 1 equiv) in dichloromethane (30 mL). The color of the reaction mixture turned from purple to blue within 5 min of stirring. The reaction mixture was allowed to stir for 1 h. Volatile materials were removed *in vacuo* and the blue residue was triturated three times with dichloromethane. The resulting solid was suspended in dichloromethane and stored at –35 °C overnight. The desired product was collected as a bright blue powder by filtration through sintered glass frit, washed with dichloromethane, and dried under vacuum. The filtrate contained one or two unidentified paramagnetic species, displaying peaks at 4.85 and 9.5 ppm in the ^{2}H NMR spectrum. Compound **2** obtained in this manner amounted to 1.188 g (1.8 mmol, 60 % yield; this amount corresponds to 53 % yield if the presence of 1 equiv CH_2Cl_2 is assumed). X-ray quality crystals were obtained from a dilute

dichloromethane solution layered with petroleum ether, upon storing at –35 °C for days. The crystals submitted to the X-ray diffraction study were prepared *via* an alternative route, starting from $(PNP^{OMe})Cr(CO)_4$. Details on this route will be reported in a subsequent paper. ^{2}H NMR (76 MHz, CH_2Cl_2) δ: 8.8 (br s, OC*D*$_3$). μ_{eff} = 3.8 μ_B. λ_{max} (CH_2Cl_2, nm): 536 (ε=269 $M^{-1}cm^{-1}$), 661 (ε=484 $M^{-1}cm^{-1}$). Anal. calcd. for $C_{29}H_{31}Cl_3NO_4P_2Cr$ (%): C, 51.38; H, 4.61; N, 2.07; for $C_{30}H_{33}Cl_5NO_4P_2Cr$ (considering the presence of one equivalent of dichloromethane in the crystal lattice, based on the findings of a single crystal X-ray diffraction study): C, 47.23; H, 4.32; N, 1.84. Found: C, 46.24; H, 4.29; N, 1.77.

Synthesis of $(PNP^{OMe})CrPh_3$ (3)

In the glove box, compound **1** (1.069 g, 2.01 mmol, 1.03 equiv) was dissolved in 75 mL of dichloromethane. Portions of $CrPh_3(THF)_3$ (974 mg, 1.95 mmol, total, 1 equiv) were added as a slurry in tetrahydrofuran (approximately 2 mL) to the stirring solution of **1** over 5 min. The reaction mixture turned a deep red color upon addition. Volatile materials were removed *in vacuo*, approximately 50 mL of dichloromethane were added, followed by solvent removal *in vacuo*. The red solid residue was dissolved in approximately 25 mL of dichloromethane and approximately 30 mL of petroleum ether were added to precipitate a red solid. This mixture was stored at –35 °C overnight. The solid material collected by filtration of the cold solution was recrystallized from a dichloromethane / petroleum ether mixture, collected on a sintered glass frit, and dried under vacuum to leave 1.050 g of **3** as a red, microcrystalline solid (66 % yield). ^{2}H NMR (RT, 76 MHz, CH_2Cl_2): δ 8.5 ppm (br s, OC*D*$_3$). Anal. calcd. for $C_{47}H_{34}D_{12}NO_4P_2Cr$ (%): C, 69.26; H, 5.70; N, 1.72. Found: C, 69.03; H, 5.69; N, 1.86. μ_{eff} = 3.8 μ_B. X-ray quality crystals of **3** were obtained from slow diffusion of petroleum ether into a concentrated CH_2Cl_2 solution of the complex at –35 °C.

Synthesis of (PNP^{OMe})CrBr(*o,o'*-biphenyldiyl) (4)

Magnesium turnings (12.3 mg, 1.4 mmol, 8 equiv) were added to a diethylether solution (10 mL) of o,o'-dibomobiphenyl (53.5 mg, 0.17 mmol, 1 equiv) and allowed to stir overnight at room temperature. The solution was decanted and concentrated to approximately 5 mL to cause precipitation of a white solid, which was dissolved by addition of dichloromethane. The resulting solution was cooled to almost freezing then added to a thawing dichloromethane

solution (20 mL) of **2** (0.1183 mg, 0.17 mmol, 1 equiv). The color of the reaction mixture gradually changed from dark blue to forest green upon warming up. The reaction mixture was allowed to stir for 2 h then volatile materials were removed *in vacuo*. Dichloromethane was added to the green residue and the mixture filtered through Celite to remove a brown solid. The green filtrate was concentrated, layered with petroleum ether, and cooled to –35 °C to cause crystallization of **4** as a green material. The green solid was collected on a sintered glass frit, washed with cold dichloromethane and dried under vacuum to provide 104.2 mg of desired product (0.12 mmol, 75 % yield). In cases when a white powder (probably magnesium salts) precipitated out along with the desired product, an additional recrystallization provided clean product. X-ray quality crystals were obtained from a dilute dichloromethane solution layered with petroleum ether, upon storing at –35°C for days. ^{2}H NMR (76 MHz, CH_2Cl_2) □: 5.8 (br s, OC*D*$_3$), 9 (v br s, OC*D*$_3$). □$_{eff}$ = 3.8 □$_B$. □$_{max}$ (CH_2Cl_2, nm): 382 (□=1937 $M^{-1}cm^{-1}$), 449 (□=809 $M^{-1}cm^{-1}$), 598 (□=364 $M^{-1}cm^{-1}$). Anal. calcd. for $C_{41}H_{39}NO_4P_2BrCr$ (%): C, 61.28; H, 4.89; N, 1.74. Found: C, 61.38; H, 4.93; N, 2.10.

Variable temperature ^{2}H NMR study of 2, 3, and 4

The experiments were performed with CH_2Cl_2 solutions. At high temperatures (fast exchange) the spectra showed one peak. Upon cooling down two decoalescence processes were observed. The higher temperature one splits the peak to two peaks (one broad found between 10-20 ppm and one sharp found in the diamagnetic region ~4 ppm) in a one to one ratio. The lower temperature decoalescence splits the broad peak mentioned above into two peaks – one broad and shifted downfield (>20 ppm) and one in the diamagnetic region (overlapping with the other diamagnetic peak for **2** and **3**). A detailed account of the exchange processes proposed to be the cause of this behavior will be given in a subsequent full paper.

General procedure for trimerization of C_2H_4 with 3 activated with $H(Et_2O)_2B[C_6H_3(CF_3)_2]_4$

In the glove box a 250 mL round bottom flask was charged with **3** (16 mg, 20 □mol, 1 equiv) and $H(Et_2O)_2B[C_6H_3(CF_3)_2]_4$ (20 mg, 20 □mol, 1 equiv), and 50 mL of toluene was added to give a pale green solution. The flask was equipped with a 180 ° needle valve, degassed on the vacuum line at –78 °C, warmed to room temperature, and backfilled with 1 atmosphere of ethylene. After 1 h the reaction was quenched with H_2O. The organic fraction was separated and filtered

through a plug of activated alumina to remove any chromium, and this mixture was analyzed by GC-MS. The reaction produces 1-hexene with a range of 700 – 2,000 turnovers in greater than 85 % overall selectivity.

Trimerization of a C_2D_4 / C_2H_4 mixture with 3 activated with $H(Et_2O)_2B[C_6H_3(CF_3)_2]_4$

Chlorobenzene was vacuum transferred into a Schlenk tube charged with **3** (18 mg, 22 μmol, 1 equiv) and $H(Et_2O)_2B[C_6H_3(CF_3)_2]_4$ (22 mg, 22 μmol, 1 equiv). A 1:1 mixture of C_2D_4 and C_2H_4 (128.2 mL at 213 torr, 1480 μmol, 67 equiv) was condensed into the tube at –192 °C (~1.8 atm at room temperature). The reaction mixture was allowed to warm to room temperature and left to stir during which time the mixture changed from a red-brown color to a green-brown color. After stirring for 1.5 hours at room temperature, the reaction was vented and quenched with H_2O. The organic fraction was separated and filtered through a plug of activated alumina to remove any chromium, and this mixture was analyzed by GC-MS. The 1-hexene fraction resolves in a quartet showing a 1:3:3:1 distribution of isotopomers (C_6H_{12}, $C_6H_8D_4$, $C_6H_4D_8$, and C_6D_{12}).

Trimerization of a C_2D_4 / C_2H_4 mixture with 4 activated with $NaB[C_6H_3(CF_3)_2]_4$

D_2-dichloromethane was vacuum transferred to a J-Young tube charged with **4** (9.2 mg, 11.4 μmol, 1 equiv) and $NaB[C_6H_3(CF_3)_2]_4$ (12.2 mg, 13.8 μmol, 1.2 equiv). The mixture was warmed up to room temperature using a water bath, followed by mixing (*via* mechanical rotation) for 10 min. The mixture turned brown upon starting materials dissolving. A 1:1 mixture of C_2D_4 and C_2H_4 (128.2 mL at 29 torr, 200 μmol, 17.5 equiv) was condensed in (~2.4 atm in the tube at room temperature). The reaction mixture was allowed to mix for 1h at room temperature during which time it achieved a brown green color. The reaction vessel was cooled in a dry ice / acetone bath and degassed. Following removal of ethylene, the mixture was allowed to reach room temperature and volatile materials were vacuum transferred to a round bottom flask and analyzed by GC-MS. The 1-hexene fraction shows a 1:3:3:1 distribution of isotopomers (C_6H_{12}, $C_6H_8D_4$, $C_6H_4D_8$, and C_6D_{12}). The solid residue was partitioned between water and dichloromethane and the organic fraction was analyzed by GC-MS to reveal the presence of d_0- and d_4-*o*-vinylbiphenyl and biphenyl.

Trimerization of a C_2D_4 / C_2H_4 mixture with 4 activated with MAO

Compound **4** (8.2 mg, 10.1 μmol, 1 equiv) was suspended in toluene (30 mL) and the mixture was cooled to –78 °C in a dry ice / acetone bath. Under counterflow of argon, the Teflon stopcock was replaced with a rubber septum, and MAO solution (10 % in toluene, d = 0.875g / mL, 2.4 mL, 300 equiv) was added *via* syringe. The septum was replaced with the Teflon

stopcock. The mixture was degassed briefly and placed under 1:1 C_2D_4 / C_2H_4 mixture (~2.3 atm static pressure, 10 mmol, 1000 equiv) while warming up to room temperature in a water bath. The reaction mixture was allowed to stir for 1.5 h. An aliquot was collected, quenched with water and analyzed by GC-MS. The 1-hexene fraction resolves in a quartet showing a 1:3:3:1 distribution of isotopomers (C_6H_{12}, $C_6H_8D_4$, $C_6H_4D_8$, and C_6D_{12}). D_0- and d_4-*o*-vinylbiphenyl do not resolve on the GC trace but are both present according to the mass spectrum.

Trimerization of a C_2D_4 / C_2H_4 mixture with $CrCl_3(THF)_3$ / PNP^{OMe} (1) activated with MAO

A solution of $CrCl_3(THF)_3$ (6 mg, 16 μmol, 1 equiv) in dichloromethane (1 mL) was added to a dichloromethane solution (1 mL) of **1** (8.3 mg, 16 μmol, 1 equiv). The reaction mixture was allowed to stir for 1 h at room temperature. Volatile materials were removed *in vacuo*, and toluene (40 ml) was added. The resulting mixture was cooled down in a dry ice / acetone bath and the Teflon stopcock was replaced with a rubber septum under counterflow of argon. MAO solution (10% in toluene, d = 0.875g/mL, 3.2 mL, 300 equiv) was added *via* syringe then the septum was replaced with the Teflon stopcock. The mixture was degassed briefly and placed under 1:1 C_2D_4 / C_2H_4 mixture (~1.4 atm static pressure at room temperature, 1.4 mmol, 875 equiv) while warming up to room temperature in a water bath. It was allowed to stir for 2.5 h; the mixture turned pale green. An aliquot was collected, quenched with water and analyzed by GC-MS. The 1-hexene fraction displays a 1:3:3:1 distribution of isotopomers (C_6H_{12}, $C_6H_8D_4$, $C_6H_4D_8$, and C_6D_{12}).

Reaction of 4 with ethylene

D_2-dichloromethane was vacuum transferred to a J-Young tube charged with **4** (8.1 mg, 10.1 μmol, 1 equiv). Ethylene (43.48 mL at 87 torr, 200 μmol, 20 equiv) was condensed in (~ 2 atm in the tube at room temperature). The mixture was warmed up to room temperature using a water bath then allowed to mix by mechanical rotation for 1 h. During this time the mixture achieved a brown-green color. *O*-vinyl-biphenyl was detected by ^{1}H NMR spectroscopy, but no 1-hexene was observed. After an additional 1 h of mixing the mixture turned brown-red, but no 1-hexene was formed according to ^{1}H NMR spectroscopy.

Trimerization of *cis*-, *trans*-, and *gem*-$C_2H_2D_2$

D_2-dichloromethane was vacuum transferred to a J-Young tube or Schlenk flask charged with **4** (8-34 mg, 10-42 μmol, 1 equiv) and $NaB[C_6H_3(CF_3)_2]_4$ (10.5-45 mg, 12-51 μmol, 1.2 equiv). The mixture was warmed up to room temperature using a water bath followed by mixing (*via* mechanical rotation for NMR tubes or magnetic stirring for flasks) for 10 min. The mixture turned brown upon starting materials dissolving. Labeled ethylene (128.2 mL at 30-125 torr, 200-860 μmol, 17.5-23 equiv) was condensed in (~2.3-3.8 atm in the vessel at room temperature). The reaction mixture was allowed to mix for 1-1.5 h at room temperature during which the mixture turned brown-green. Subsequently, the reaction mixture was cooled in a dry ice / acetone bath and degassed. Following removal of ethylene, the mixture was allowed to warm to room temperature, and volatile materials were vacuum transferred to a round bottom flask and analyzed by ^1H and ^{13}C NMR spectroscopy. The solid residue was partitioned between water and dichloromethane and the organic fraction was analyzed by GC-MS to reveal the presence of d_2-*o*-vinylbiphenyl and biphenyl. ^{13}C NMR of 1-hexenes resulted from the trimerization of *trans*-$C_2H_2D_2$ (126 MHz, CD_2Cl_2) δ: 139.8 (s, =*C*H) 139.4 (t, =*C*D), 114.1 and 114.0 (t, RHC=*C*HD and RDC=*C*HD), 33.4 (t, *C*HD), 31.1 (t, *C*HD), 22.2 (t, *C*HD), 13.8 (t, *C*H_2D).

The isotope effects for 1-hexene formation were determined from the integrals of the peaks in the olefinic region (see Table 1 for actual values and section S3 for examples). At this time, it is not clear what is the cause of isotope effect variation with the type of vessel used for the reaction. Generation of the six possible double bond d_1- and d_2-isotopomers of 1-hexene (1,2-*cis* and *trans*-d_2 and h_2-1-hexene and 1,1-d_2 and h_2-1-hexene) provided access to their spectroscopic features in the olefinic region of the ^1H NMR spectrum (Figure 1, see also section S3).

	Cis-$C_2H_2D_2$			*Trans*-$C_2H_2D_2$	*Gem*-$C_2H_2D_2$	
NMR tube (RT)	3.5		3.1	3.4	0.9	0.9
10 mL RB Schlenk flask (RT)	2.3		---	---	---	
5 mL Schlenk tube (Temp - K)	2.4 (298)	2.5 (273)	3.4 (248)	---	1.3	

Table 1. Isotope effects for the trimerization of different isomers of dideuteroethylene under various reaction conditions.

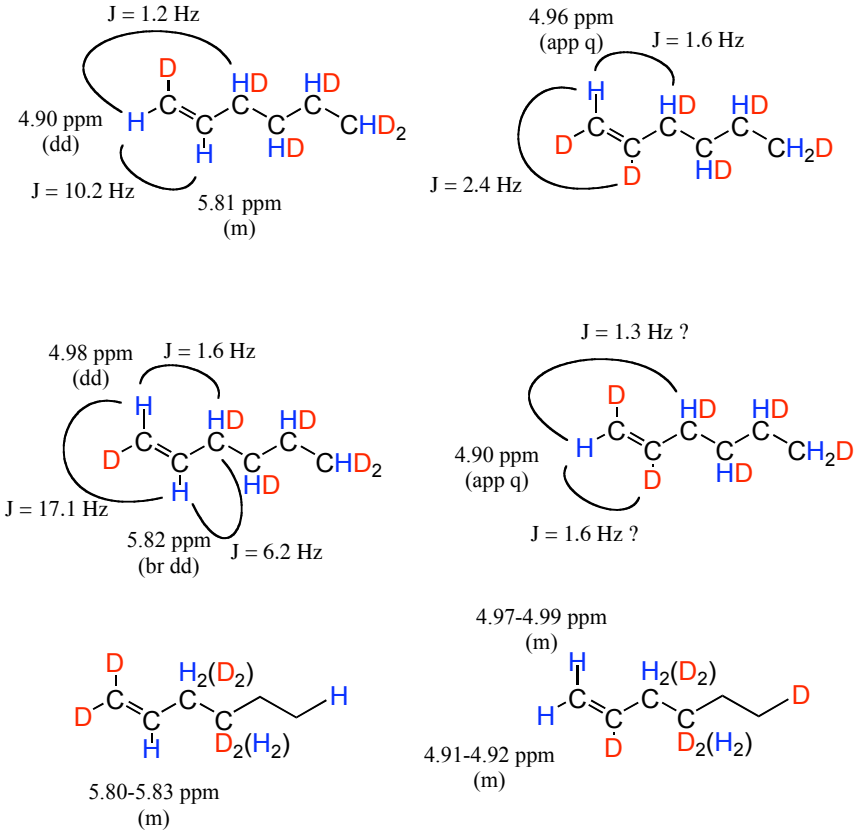
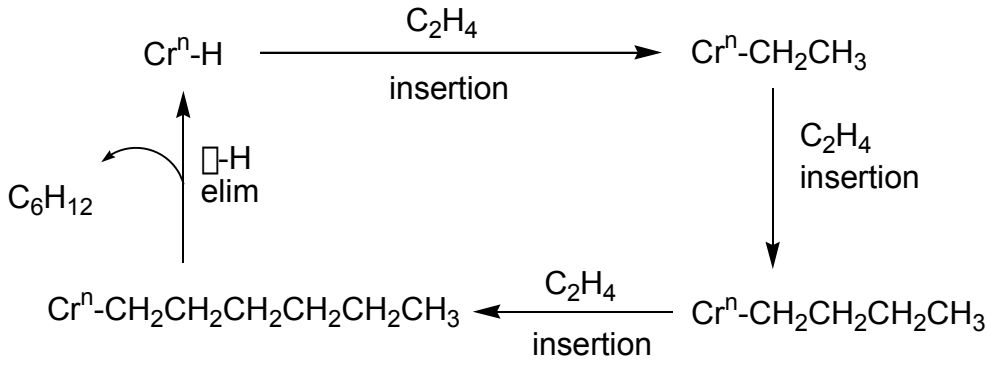
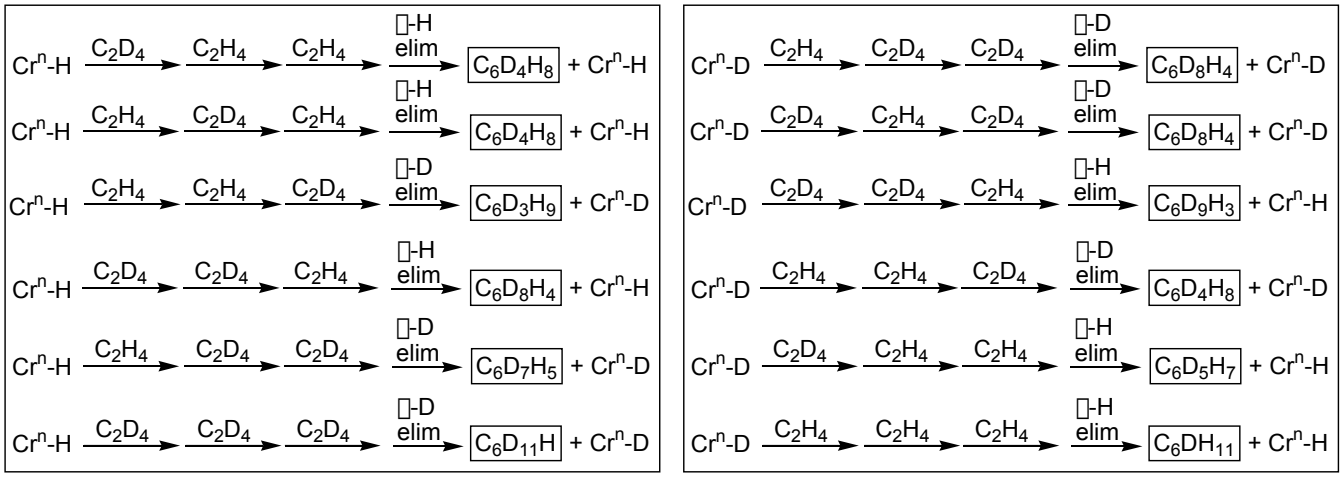


Figure 1. ^{1}H NMR data (CD_2Cl_2, 500 MHz) for the olefinic protons of various isotopomers of 1-hexene-d_6.

S2. *Cossee-type and redox mechanisms for the formation of 1-hexene from ethylene. Expected outcomes and experimental data for the trimerization of a 1:1 mixture of C_2D_4 and C_2H_4*



Scheme 1. Proposed Cossee-type mechanism for 1-hexene formation from ethylene.



$C_6D_{12} : C_6D_{11}H : C_6D_9H_3 : C_6D_8H_4 : C_6D_7H_5 : C_6D_5H_7 : C_6D_4H_8 : C_6D_3H_9 : C_6DH_{11} : C_6H_{12} =$
$1 : 1 : 1 : 3 : 2 : 2 : 3 : 1 : 1 : 1$

Figure 2. Some hexenes that could form from a C_2D_4 / C_2H_4.mixture *via* a Cossee-type mechanism (top). List of all expected isotopomers and their statistical distribution for a Cossee-type mechanism (bottom).

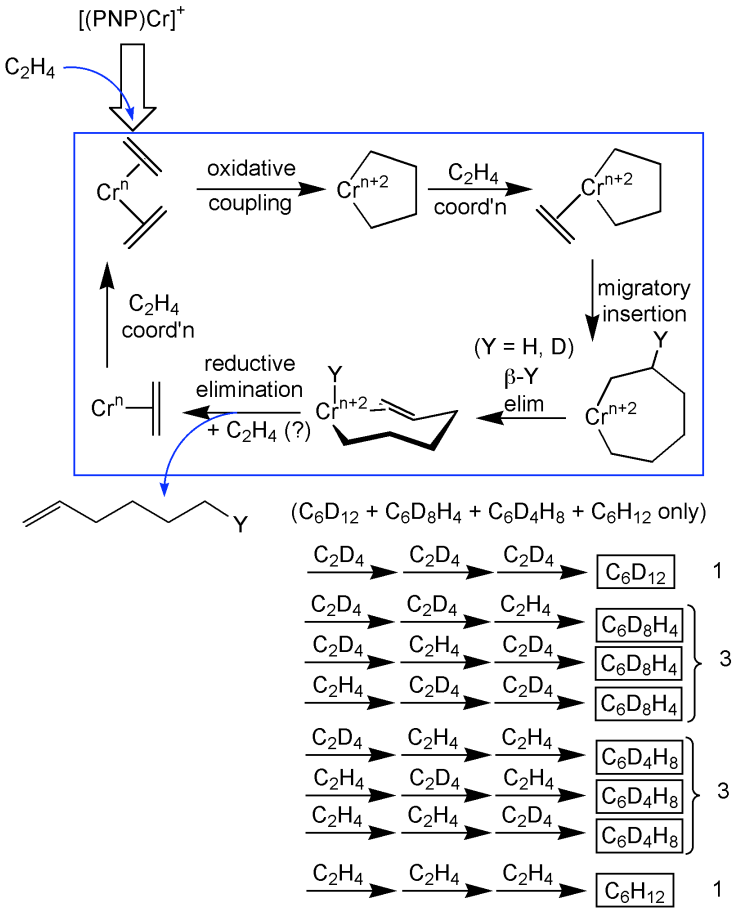


Figure 3. Proposed mechanism for 1-hexene formation from a 1:1 C_2D_4 / C_2H_4.mixture involving metallacyclic intermediates (top) and expected isotopomer distribution (bottom).

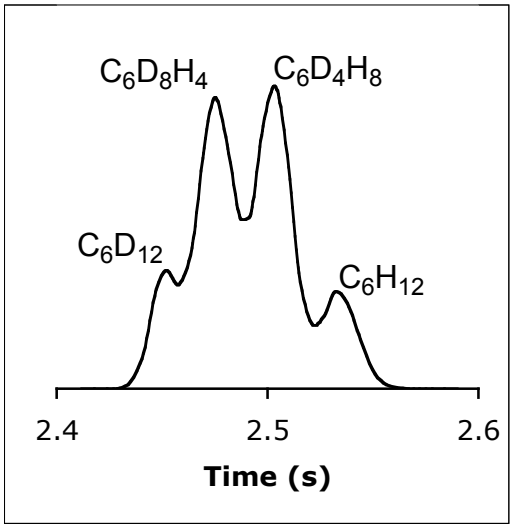


Figure 4. GC data of the 1-hexene fraction obtained from trimerization of a 1:1 mixture of C_2D_4 and C_2H_4

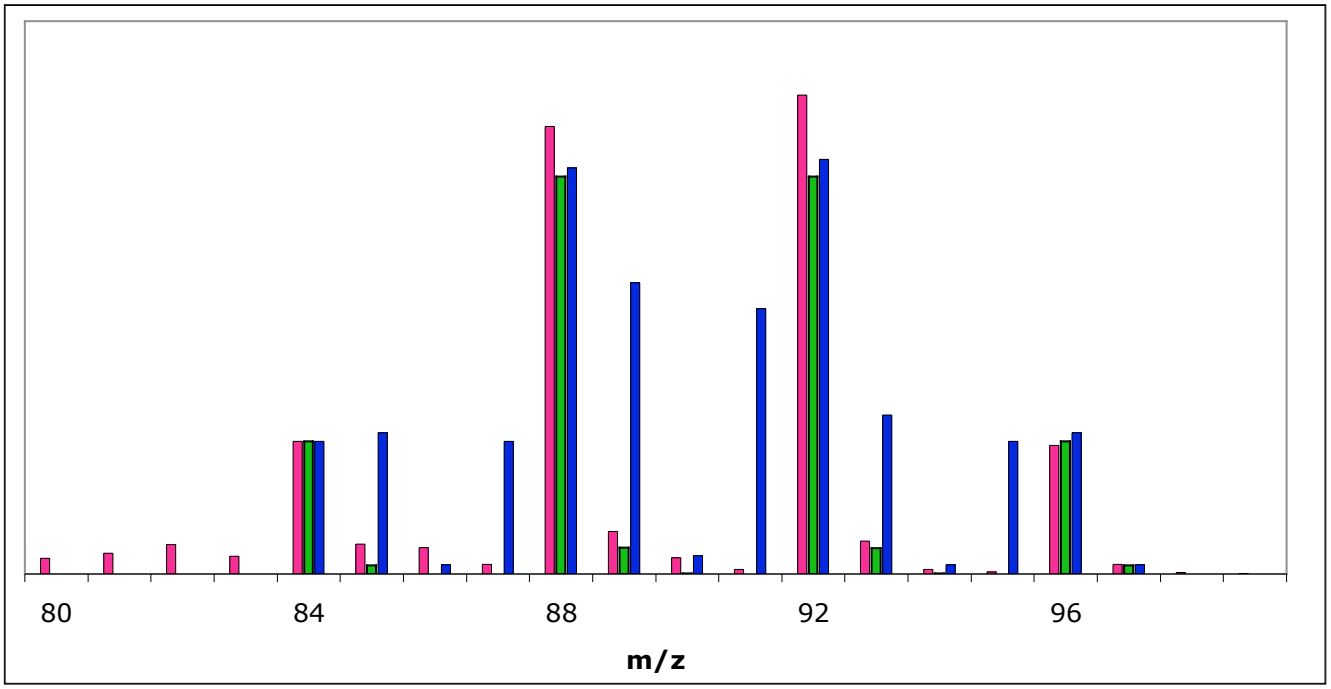


Figure 5. MS data (red) of the 1-hexene fraction obtained from trimerization of a 1:1 mixture of C_2D_4 and C_2H_4. Simulations of expected isotopomer distributions for a mechanism involving metallacyclic intermediates and for a Cossee-type mechanism are presented in green and blue, respectively.[4]

S3. Trimerization of cis-, trans- and gem-dideuteroethylene – ^{1}H NMR spectra of the volatile fraction

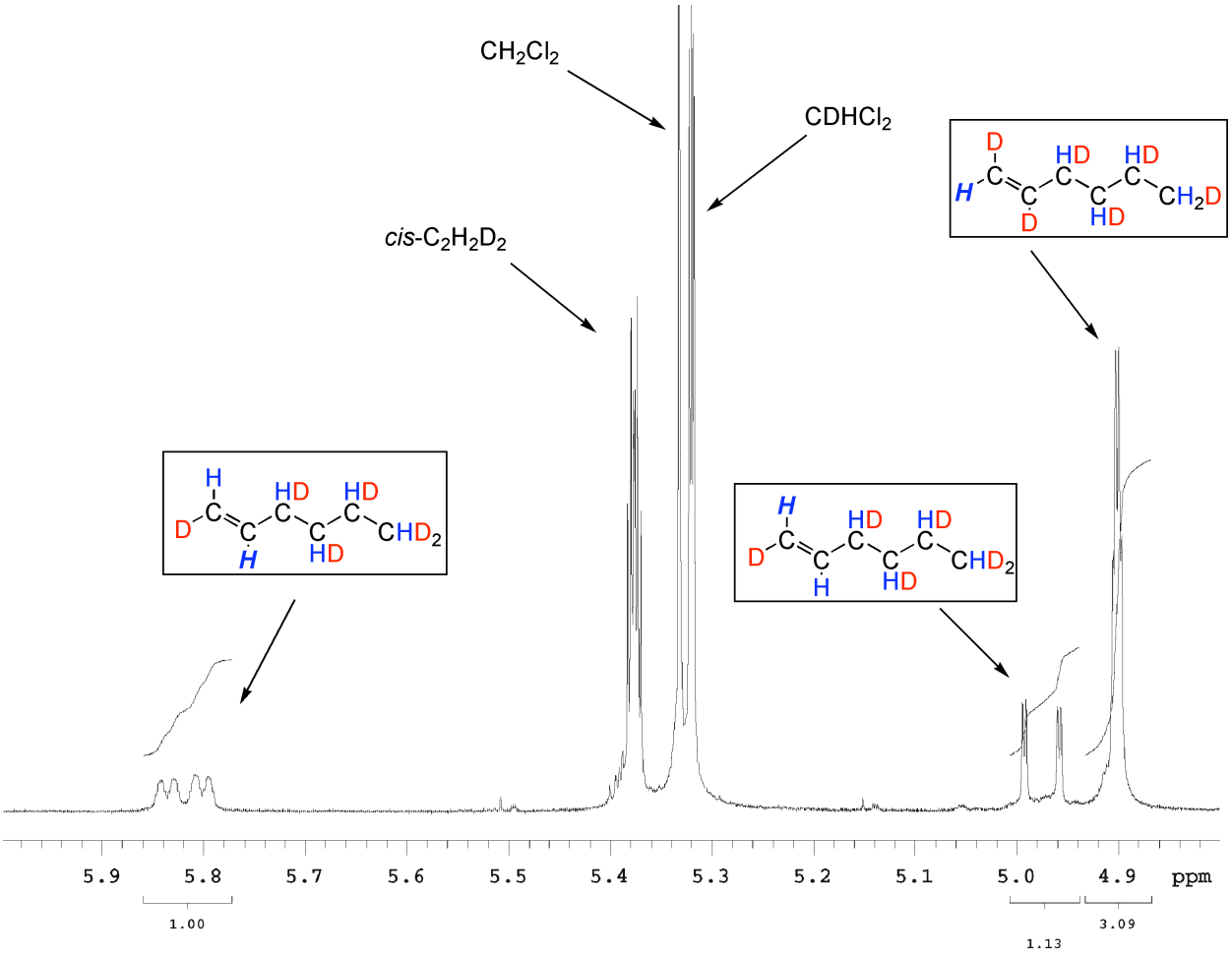


Figure 6. Olefinic region of the ^{1}H NMR spectrum of the volatile materials resulting from the trimerization of *cis*-dideuteroethylene.

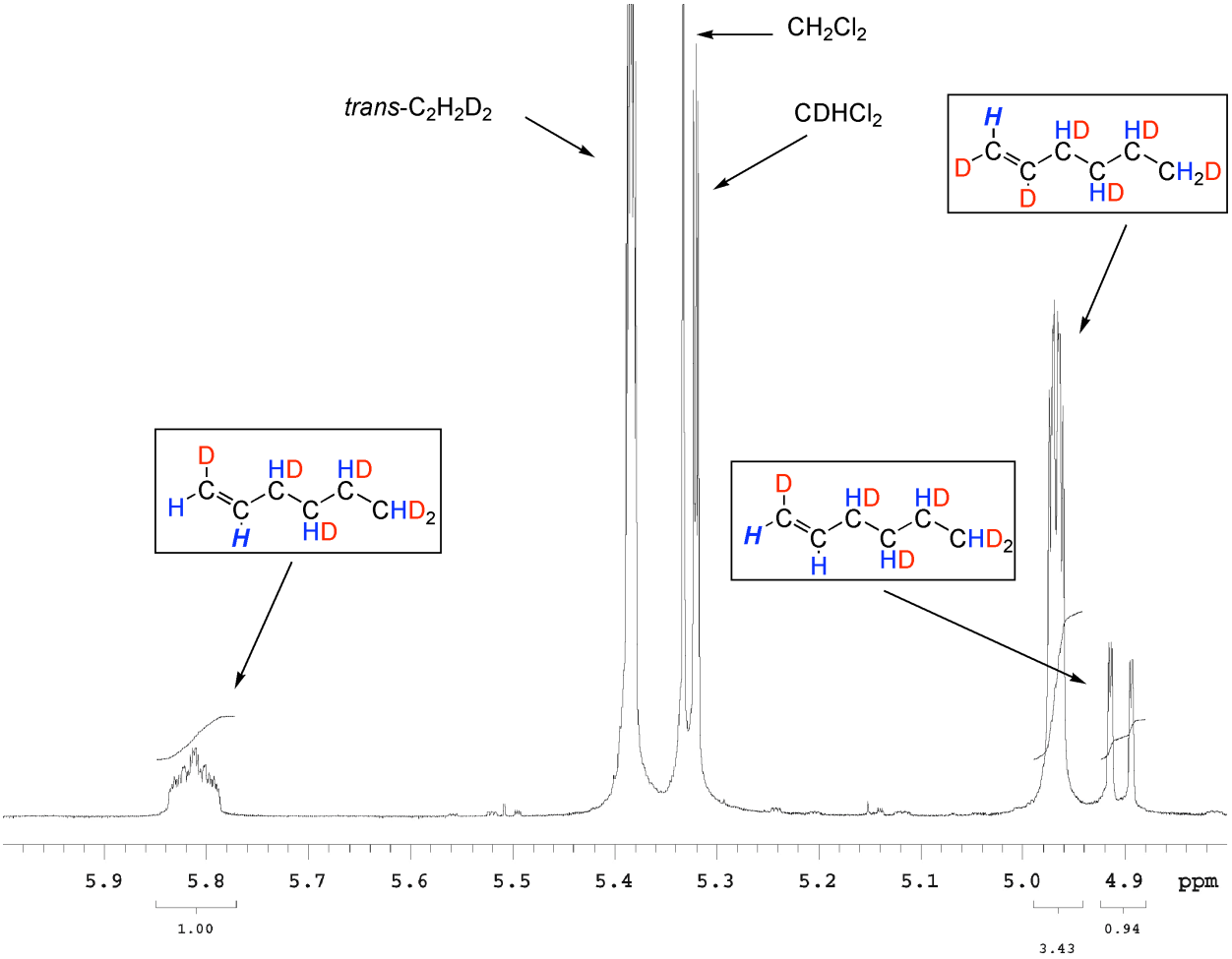


Figure 7. Olefinic region of the ^{1}H NMR spectrum of the volatile materials resulting from the trimerization of *trans*-dideuteroethylene.

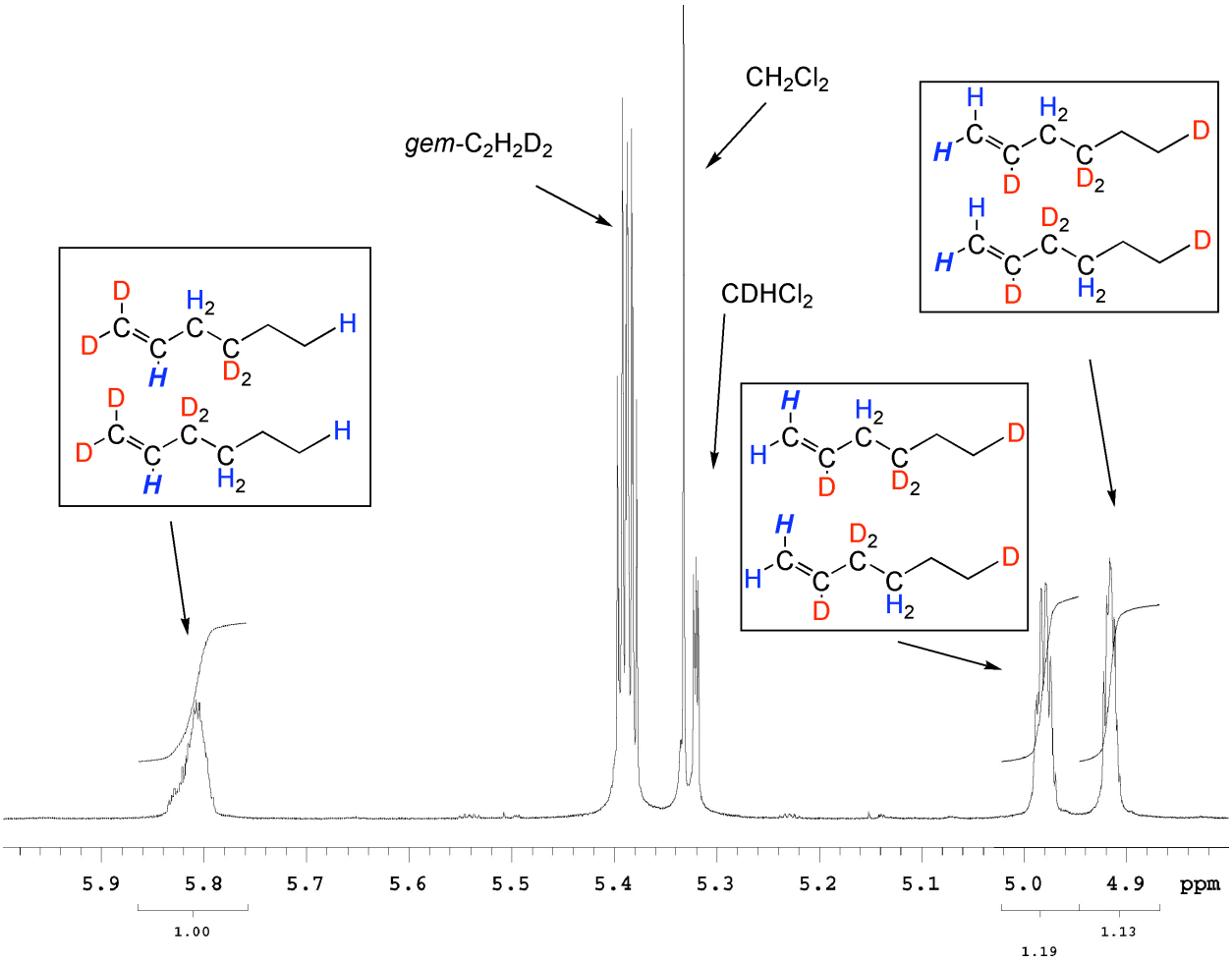


Figure 8. Olefinic region of the ^{1}H NMR spectrum of the volatile materials resulting from the trimerization of *gem*-dideuteroethylene.

S4. *Expected isotopomeric isomers and isotope effects for the trimerization of cis- and gem-dideuteroethylene depending on the mechanism*

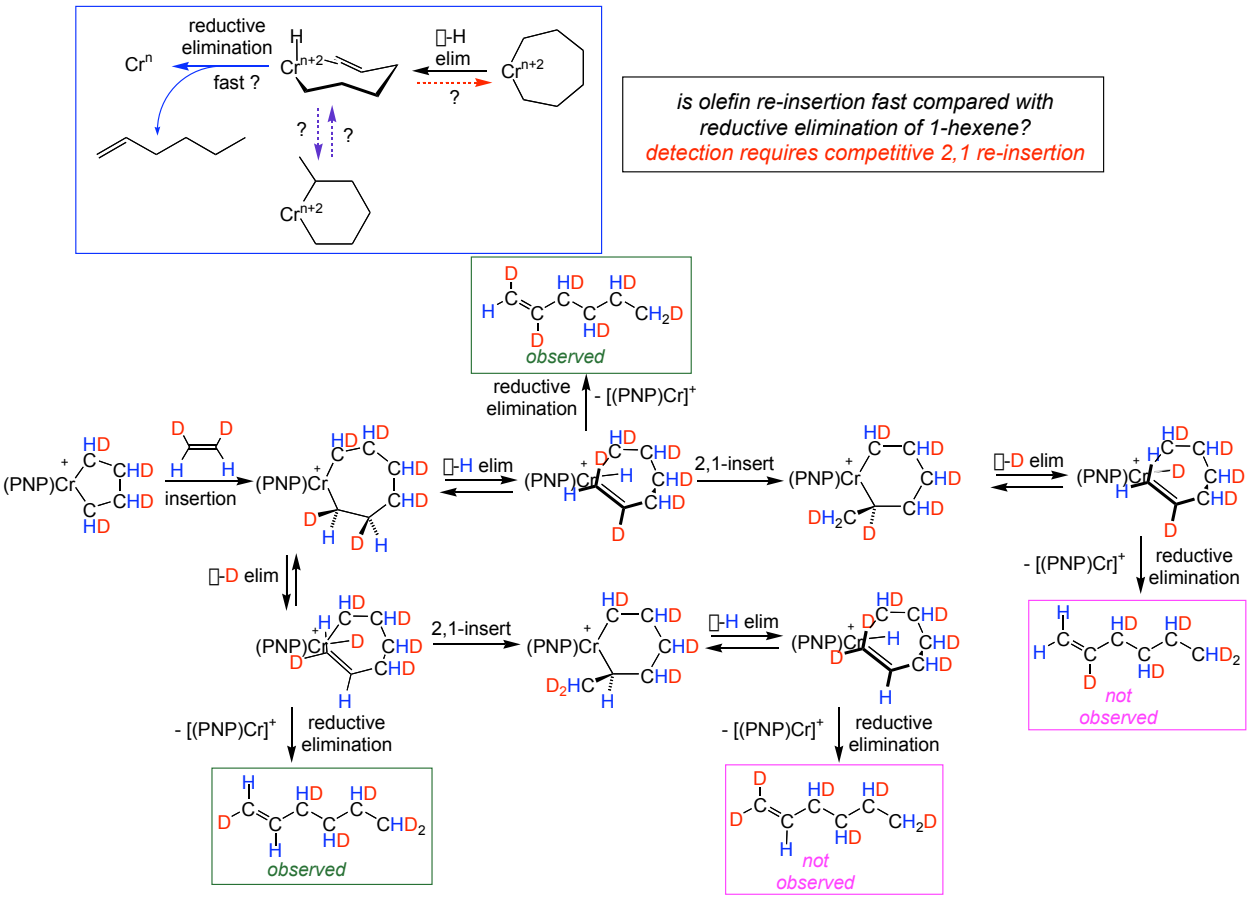


Figure 9. Possible isotopomeric isomers of 1-hexene from mechanism involving 2,1 re-insertion that is competitive with reductive elimination.

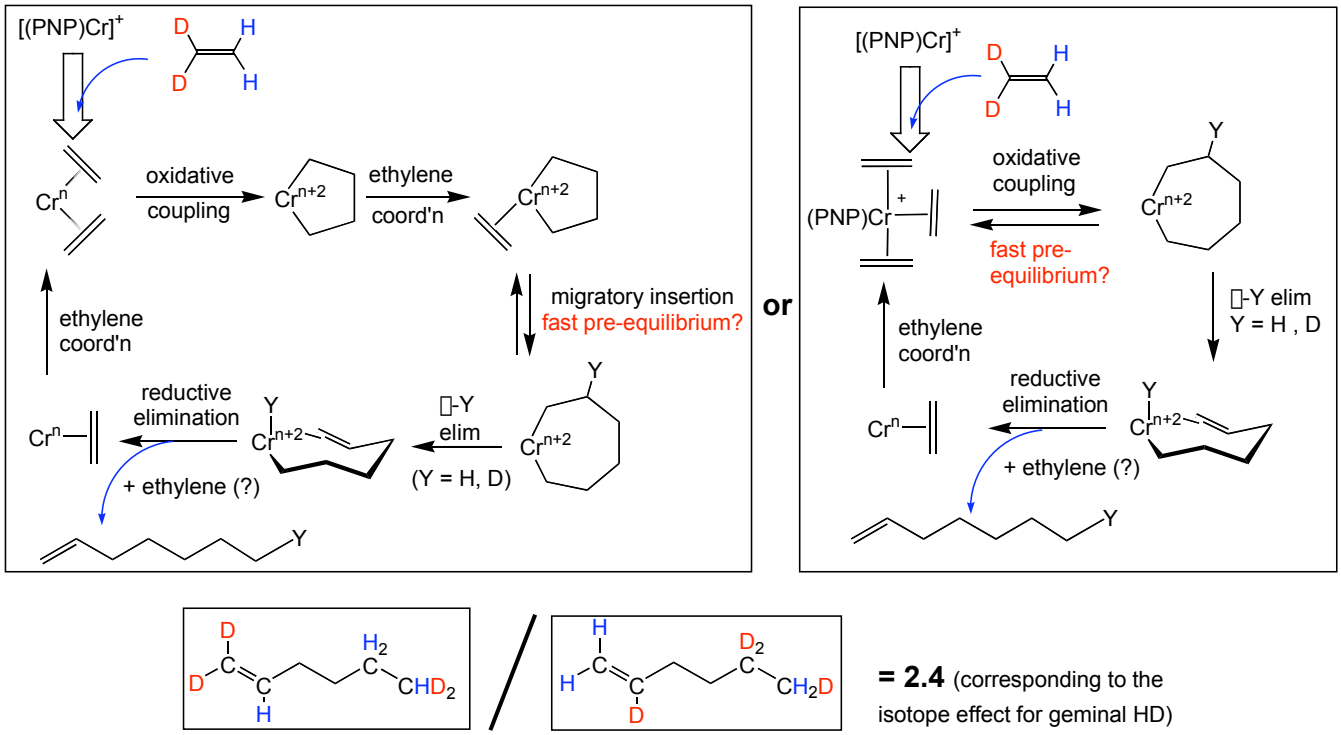


Figure 10. Proposed mechanisms involving reversible formation of the metallacycloheptane (top). Expected isotope effect for the trimerization of *gem*-dideuteroethylene would correspond to the one observed for the trimerization of *cis*- or *trans*-dideuteroethylene, *i. e.* coming from the β-hydride abstraction / reductive elimination steps (bottom).

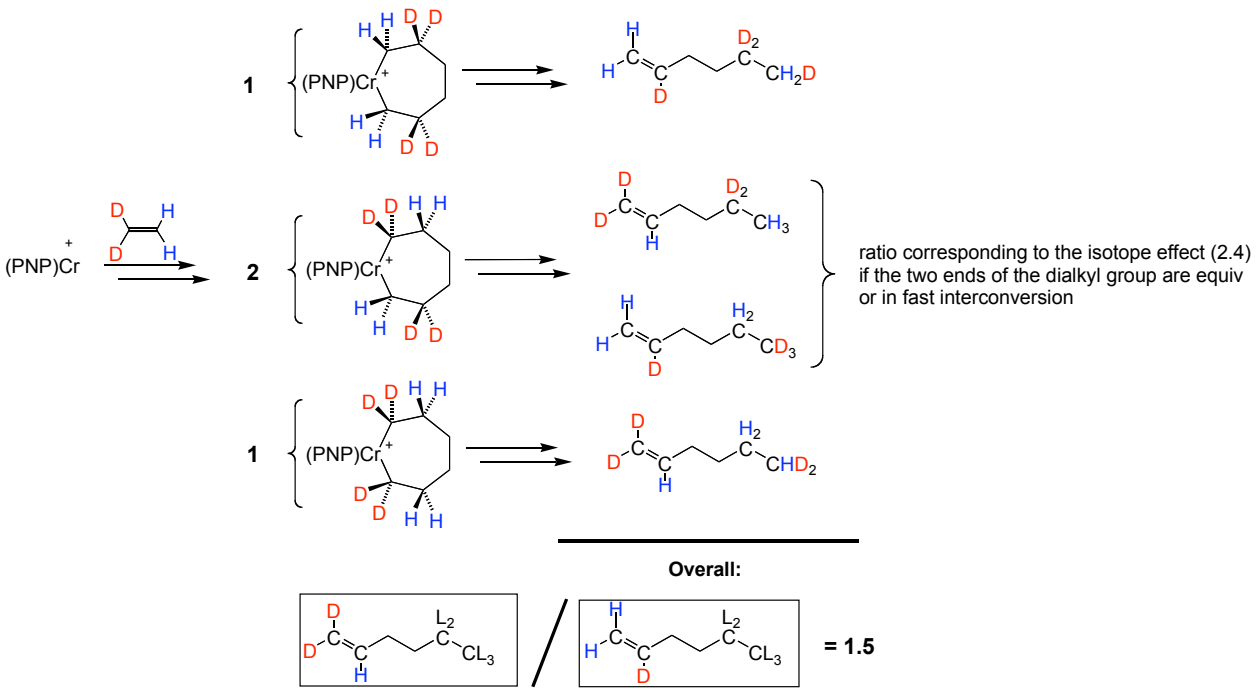


Figure 11. Expected isotopomer distribution from the trimerization of *gem*-dideuteroethylene for a mechanism involving irreversible formation of the metallacycloheptane and equivalent ends of the alkyl group.

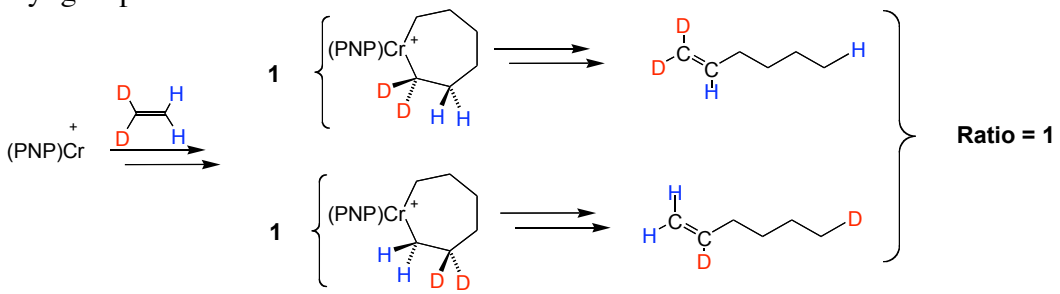


Figure 12. Expected isotopomer distribution from the trimerization of *gem*-dideuteroethylene for a mechanism involving irreversible formation of the metallacycloheptane and selective β-hydride abstraction / reductive elimination from only one end of the dialkyl group (see Figure 10).

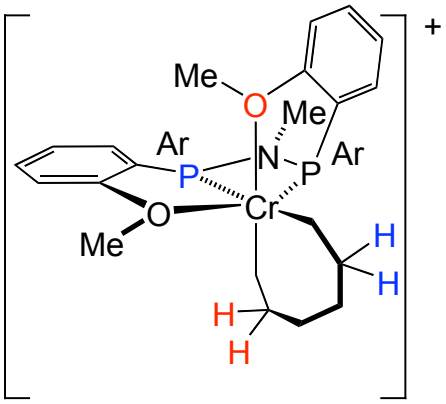


Figure 13. Drawing of the proposed metallacycloheptane intermediate displaying inequivalent ends of the alkanediyl group.

S5. *Structural drawings, tables with structural parameters, and crystallographic information for* ***2***, ***3***, *and* ***4***

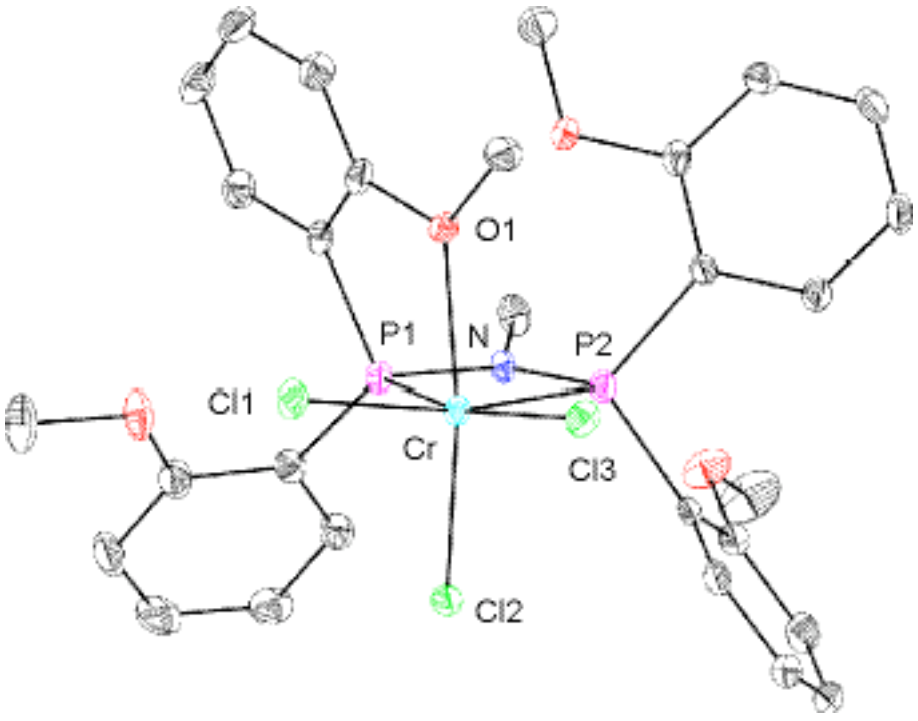


Figure 14. Structural drawing of **2** with thermal ellipsoids at the 50% probability level.

Table 2. Crystal data and structure refinement for 2 (CCDC 205652).

Empirical formula	$C_{29}H_{31}Cl_3NO_4P_2Cr \cdot CH_2Cl_2$
Formula weight	762.76
Crystallization Solvent	Dichloromethane / petroleum ether
Crystal Habit	Plate
Crystal size	0.28 x 0.27 x 0.07 mm^3
Crystal color	Dark Blue

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 16551 reflections used in lattice determination	2.22 to 28.12°
Unit cell dimensions	a = 10.6977(7) Å b = 15.0041(10) Å β = 96.1720(10)° c = 21.4755(14) Å
Volume	3427.0(4) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.478 Mg/m^3
F(000)	1564
Data collection program	Bruker SMART v5.054
θ range for data collection	1.66 to 28.17°
Completeness to θ = 28.17°	93.1 %
Index ranges	$-14 \le h \le 14$, $-19 \le k \le 18$, $-28 \le l \le 28$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	48014
Independent reflections	7838 [R_{int} = 0.0696]
Absorption coefficient	0.853 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9427 and 0.7962

Table 2 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7838 / 0 / 520
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.579
Final R indices [I>2□(I), 5783 reflections]	R1 = 0.0370, *w*R2 = 0.0621
R indices (all data)	R1 = 0.0618, *w*R2 = 0.0649
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/□^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.665 and -0.450 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2□(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 2 (CCDC 205652). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cr(1)	5993(1)	6899(1)	777(1)	12(1)
Cl(1)	5211(1)	7029(1)	-256(1)	17(1)
Cl(2)	7360(1)	8061(1)	760(1)	15(1)
Cl(3)	7455(1)	5779(1)	678(1)	17(1)
P(1)	4517(1)	7857(1)	1199(1)	12(1)
P(2)	6178(1)	6898(1)	1952(1)	12(1)

O(1)	4385(1)	6057(1)	856(1)	14(1)
O(2)	3344(2)	8854(1)	130(1)	25(1)
O(3)	6667(2)	7911(1)	3180(1)	25(1)
O(4)	3670(1)	5966(1)	2133(1)	17(1)
N(1)	4982(2)	7640(1)	1962(1)	12(1)
C(1)	4472(3)	5087(2)	813(1)	20(1)
C(2)	3161(2)	6409(2)	801(1)	15(1)
C(3)	3046(2)	7298(2)	982(1)	13(1)
C(4)	1854(2)	7669(2)	958(1)	18(1)
C(5)	798(2)	7175(2)	762(1)	22(1)
C(6)	938(2)	6300(2)	579(1)	22(1)
C(7)	2120(2)	5910(2)	585(1)	19(1)
C(8)	4321(2)	9043(2)	1142(1)	15(1)
C(9)	4830(2)	9588(2)	1629(1)	18(1)
C(10)	4769(2)	10511(2)	1577(1)	24(1)
C(11)	4209(3)	10881(2)	1034(1)	29(1)
C(12)	3714(3)	10366(2)	536(1)	27(1)
C(13)	3771(2)	9435(2)	585(1)	20(1)
C(14)	2760(3)	9220(2)	-447(1)	35(1)
C(15)	7647(2)	7332(1)	2341(1)	14(1)
C(16)	8729(2)	7161(2)	2057(1)	17(1)
C(17)	9896(2)	7431(2)	2331(1)	19(1)
C(18)	9989(2)	7884(2)	2894(1)	22(1)
C(19)	8930(2)	8062(2)	3186(1)	22(1)
C(20)	7755(2)	7782(2)	2914(1)	18(1)
C(21)	6757(3)	8388(2)	3767(2)	39(1)
C(22)	5856(2)	5944(1)	2440(1)	13(1)
C(23)	6890(2)	5529(2)	2777(1)	17(1)
C(24)	6740(2)	4812(2)	3167(1)	20(1)
C(25)	5548(2)	4518(2)	3250(1)	20(1)
C(26)	4507(2)	4908(2)	2920(1)	19(1)
C(27)	4656(2)	5597(2)	2501(1)	15(1)
C(28)	2436(2)	5695(2)	2238(1)	24(1)
C(29)	4202(3)	7830(2)	2472(1)	18(1)
Cl(4)	3217(1)	8579(1)	3856(1)	32(1)
Cl(5)	4123(1)	6760(1)	4097(1)	45(1)
C(31)	3336(3)	7674(2)	4385(1)	29(1)

Table 4. Selected bond lengths [Å] and angles [°] for 2 (CCDC 205652).

Cr(1)-O(1)	2.1562(15)
Cr(1)-Cl(2)	2.2776(6)
Cr(1)-Cl(1)	2.2937(6)
Cr(1)-Cl(3)	2.3210(7)
Cr(1)-P(1)	2.3855(7)
Cr(1)-P(2)	2.5098(7)
O(1)-Cr(1)-Cl(2)	165.62(4)
O(1)-Cr(1)-Cl(1)	85.10(4)
Cl(2)-Cr(1)-Cl(1)	95.06(2)
O(1)-Cr(1)-Cl(3)	97.71(4)
Cl(2)-Cr(1)-Cl(3)	96.48(2)
Cl(1)-Cr(1)-Cl(3)	98.79(2)
O(1)-Cr(1)-P(1)	75.92(4)
Cl(2)-Cr(1)-P(1)	89.82(2)
Cl(1)-Cr(1)-P(1)	97.39(2)
Cl(3)-Cr(1)-P(1)	162.03(3)
O(1)-Cr(1)-P(2)	84.11(4)
Cl(2)-Cr(1)-P(2)	92.01(2)
Cl(1)-Cr(1)-P(2)	162.47(3)
Cl(3)-Cr(1)-P(2)	96.31(2)
P(1)-Cr(1)-P(2)	66.56(2)

Table 5. Bond lengths [Å] and angles [°] for 2 (CCDC 205652).

Cr(1)-O(1)	2.1562(15)	C(17)-C(18)	1.381(3)
Cr(1)-Cl(2)	2.2776(6)	C(17)-H(17)	0.93(2)
Cr(1)-Cl(1)	2.2937(6)	C(18)-C(19)	1.379(4)
Cr(1)-Cl(3)	2.3210(7)	C(18)-H(18)	0.93(2)
Cr(1)-P(1)	2.3855(7)	C(19)-C(20)	1.393(3)
Cr(1)-P(2)	2.5098(7)	C(19)-H(19)	0.87(2)
P(1)-N(1)	1.6920(18)	C(21)-H(21A)	0.97(3)
P(1)-C(3)	1.800(2)	C(21)-H(21B)	1.01(3)
P(1)-C(8)	1.794(2)	C(21)-H(21C)	1.06(3)
P(1)-P(2)	2.6884(8)	C(22)-C(27)	1.404(3)
P(2)-N(1)	1.6978(18)	C(22)-C(23)	1.400(3)
P(2)-C(15)	1.820(2)	C(23)-C(24)	1.384(3)
P(2)-C(22)	1.829(2)	C(23)-H(23)	1.00(2)
O(1)-C(2)	1.404(3)	C(24)-C(25)	1.379(3)
O(1)-C(1)	1.462(3)	C(24)-H(24)	0.96(2)
O(2)-C(13)	1.351(3)	C(25)-C(26)	1.384(3)
O(2)-C(14)	1.436(3)	C(25)-H(25)	0.95(2)
O(3)-C(20)	1.363(3)	C(26)-C(27)	1.391(3)
O(3)-C(21)	1.444(3)	C(26)-H(26)	0.94(2)
O(4)-C(27)	1.366(2)	C(28)-H(28A)	0.98(3)
O(4)-C(28)	1.422(3)	C(28)-H(28B)	0.98(2)
N(1)-C(29)	1.475(3)	C(28)-H(28C)	0.96(3)
C(1)-H(1A)	0.97(2)	C(29)-H(29A)	0.96(3)
C(1)-H(1B)	0.94(2)	C(29)-H(29B)	0.95(2)
C(1)-H(1C)	0.99(2)	C(29)-H(29C)	0.97(2)
C(2)-C(7)	1.379(3)	Cl(4)-C(31)	1.767(3)
C(2)-C(3)	1.399(3)	Cl(5)-C(31)	1.756(3)
C(3)-C(4)	1.388(3)	C(31)-H(31A)	0.88(3)
C(4)-C(5)	1.379(3)	C(31)-H(31B)	0.99(3)
C(4)-H(4)	0.91(2)		
C(5)-C(6)	1.383(4)	O(1)-Cr(1)-Cl(2)	165.62(4)
C(5)-H(5)	0.87(2)	O(1)-Cr(1)-Cl(1)	85.10(4)
C(6)-C(7)	1.392(3)	Cl(2)-Cr(1)-Cl(1)	95.06(2)
C(6)-H(6)	0.87(2)	O(1)-Cr(1)-Cl(3)	97.71(4)
C(7)-H(7)	0.96(2)	Cl(2)-Cr(1)-Cl(3)	96.48(2)
C(8)-C(13)	1.404(3)	Cl(1)-Cr(1)-Cl(3)	98.79(2)
C(8)-C(9)	1.392(3)	O(1)-Cr(1)-P(1)	75.92(4)
C(9)-C(10)	1.391(3)	Cl(2)-Cr(1)-P(1)	89.82(2)
C(9)-H(9)	0.91(2)	Cl(1)-Cr(1)-P(1)	97.39(2)
C(10)-C(11)	1.370(4)	Cl(3)-Cr(1)-P(1)	162.03(3)
C(10)-H(10)	0.92(2)	O(1)-Cr(1)-P(2)	84.11(4)
C(11)-C(12)	1.377(4)	Cl(2)-Cr(1)-P(2)	92.01(2)
C(11)-H(11)	0.95(3)	Cl(1)-Cr(1)-P(2)	162.47(3)
C(12)-C(13)	1.403(3)	Cl(3)-Cr(1)-P(2)	96.31(2)
C(12)-H(12)	0.90(2)	P(1)-Cr(1)-P(2)	66.56(2)
C(14)-H(14A)	1.04(2)	N(1)-P(1)-C(3)	108.57(9)
C(14)-H(14B)	0.90(2)	N(1)-P(1)-C(8)	106.11(10)
C(14)-H(14C)	1.04(3)	C(3)-P(1)-C(8)	110.63(11)
C(15)-C(20)	1.398(3)	N(1)-P(1)-Cr(1)	96.53(7)
C(15)-C(16)	1.389(3)	C(3)-P(1)-Cr(1)	102.51(7)
C(16)-C(17)	1.384(3)	C(8)-P(1)-Cr(1)	130.46(8)
C(16)-H(16)	0.93(2)	N(1)-P(1)-P(2)	37.60(6)

C(3)-P(1)-P(2)	114.12(7)	C(9)-C(10)-H(10)	120.8(16)
C(8)-P(1)-P(2)	129.57(8)	C(10)-C(11)-C(12)	122.0(3)
Cr(1)-P(1)-P(2)	58.93(2)	C(10)-C(11)-H(11)	119.9(16)
N(1)-P(2)-C(15)	111.99(10)	C(12)-C(11)-H(11)	117.9(16)
N(1)-P(2)-C(22)	108.51(10)	C(11)-C(12)-C(13)	119.4(2)
C(15)-P(2)-C(22)	102.89(10)	C(11)-C(12)-H(12)	126.1(16)
N(1)-P(2)-Cr(1)	91.95(6)	C(13)-C(12)-H(12)	114.4(16)
C(15)-P(2)-Cr(1)	115.60(8)	O(2)-C(13)-C(8)	115.1(2)
C(22)-P(2)-Cr(1)	125.32(7)	O(2)-C(13)-C(12)	125.5(2)
N(1)-P(2)-P(1)	37.45(6)	C(8)-C(13)-C(12)	119.5(2)
C(15)-P(2)-P(1)	124.53(7)	O(2)-C(14)-H(14A)	109.8(13)
C(22)-P(2)-P(1)	127.68(8)	O(2)-C(14)-H(14B)	104.7(14)
Cr(1)-P(2)-P(1)	54.504(19)	H(14A)-C(14)-H(14B)	115(2)
C(2)-O(1)-C(1)	115.70(18)	O(2)-C(14)-H(14C)	107.5(14)
C(2)-O(1)-Cr(1)	121.19(13)	H(14A)-C(14)-H(14C)	114.2(18)
C(1)-O(1)-Cr(1)	121.45(14)	H(14B)-C(14)-H(14C)	105(2)
C(13)-O(2)-C(14)	117.3(2)	C(20)-C(15)-C(16)	118.9(2)
C(20)-O(3)-C(21)	117.1(2)	C(20)-C(15)-P(2)	124.23(18)
C(27)-O(4)-C(28)	117.68(19)	C(16)-C(15)-P(2)	116.83(18)
C(29)-N(1)-P(1)	123.47(15)	C(17)-C(16)-C(15)	121.0(2)
C(29)-N(1)-P(2)	128.55(15)	C(17)-C(16)-H(16)	118.4(14)
P(1)-N(1)-P(2)	104.95(10)	C(15)-C(16)-H(16)	120.6(14)
O(1)-C(1)-H(1A)	106.1(14)	C(16)-C(17)-C(18)	119.6(2)
O(1)-C(1)-H(1B)	105.5(13)	C(16)-C(17)-H(17)	118.5(13)
H(1A)-C(1)-H(1B)	113.5(18)	C(18)-C(17)-H(17)	121.7(13)
O(1)-C(1)-H(1C)	108.3(13)	C(17)-C(18)-C(19)	120.6(2)
H(1A)-C(1)-H(1C)	115.2(19)	C(17)-C(18)-H(18)	120.2(15)
H(1B)-C(1)-H(1C)	107.7(18)	C(19)-C(18)-H(18)	119.2(15)
C(7)-C(2)-C(3)	121.2(2)	C(20)-C(19)-C(18)	120.0(2)
C(7)-C(2)-O(1)	122.4(2)	C(20)-C(19)-H(19)	118.9(16)
C(3)-C(2)-O(1)	116.4(2)	C(18)-C(19)-H(19)	121.0(16)
C(4)-C(3)-C(2)	118.8(2)	O(3)-C(20)-C(19)	123.7(2)
C(4)-C(3)-P(1)	126.61(18)	O(3)-C(20)-C(15)	116.3(2)
C(2)-C(3)-P(1)	114.60(17)	C(19)-C(20)-C(15)	120.0(2)
C(3)-C(4)-C(5)	120.9(2)	O(3)-C(21)-H(21A)	114.4(17)
C(3)-C(4)-H(4)	118.9(14)	O(3)-C(21)-H(21B)	108.0(17)
C(5)-C(4)-H(4)	120.2(14)	H(21A)-C(21)-H(21B)	106(2)
C(6)-C(5)-C(4)	119.1(2)	O(3)-C(21)-H(21C)	108.6(14)
C(6)-C(5)-H(5)	121.0(16)	H(21A)-C(21)-H(21C)	109(2)
C(4)-C(5)-H(5)	119.8(16)	H(21B)-C(21)-H(21C)	111(2)
C(5)-C(6)-C(7)	121.5(2)	C(27)-C(22)-C(23)	117.8(2)
C(5)-C(6)-H(6)	122.2(15)	C(27)-C(22)-P(2)	125.00(17)
C(7)-C(6)-H(6)	116.3(15)	C(23)-C(22)-P(2)	117.20(17)
C(2)-C(7)-C(6)	118.4(2)	C(24)-C(23)-C(22)	121.4(2)
C(2)-C(7)-H(7)	121.4(14)	C(24)-C(23)-H(23)	119.6(12)
C(6)-C(7)-H(7)	120.3(14)	C(22)-C(23)-H(23)	119.0(12)
C(13)-C(8)-C(9)	119.3(2)	C(23)-C(24)-C(25)	119.8(2)
C(13)-C(8)-P(1)	120.57(18)	C(23)-C(24)-H(24)	118.8(15)
C(9)-C(8)-P(1)	119.85(17)	C(25)-C(24)-H(24)	121.4(15)
C(8)-C(9)-C(10)	120.9(2)	C(26)-C(25)-C(24)	120.2(2)
C(8)-C(9)-H(9)	119.9(13)	C(26)-C(25)-H(25)	118.8(14)
C(10)-C(9)-H(9)	119.2(13)	C(24)-C(25)-H(25)	121.0(14)
C(11)-C(10)-C(9)	118.9(3)	C(25)-C(26)-C(27)	120.2(2)
C(11)-C(10)-H(10)	120.1(15)	C(25)-C(26)-H(26)	118.1(13)

C(27)-C(26)-H(26)	121.7(13)	N(1)-C(29)-H(29B)	109.9(14)
O(4)-C(27)-C(26)	122.7(2)	H(29A)-C(29)-H(29B)	111(2)
O(4)-C(27)-C(22)	116.95(19)	N(1)-C(29)-H(29C)	108.2(14)
C(26)-C(27)-C(22)	120.4(2)	H(29A)-C(29)-H(29C)	107(2)
O(4)-C(28)-H(28A)	110.0(15)	H(29B)-C(29)-H(29C)	108(2)
O(4)-C(28)-H(28B)	105.7(14)	Cl(5)-C(31)-Cl(4)	112.21(15)
H(28A)-C(28)-H(28B)	111(2)	Cl(5)-C(31)-H(31A)	108.5(18)
O(4)-C(28)-H(28C)	110.8(15)	Cl(4)-C(31)-H(31A)	111.1(18)
H(28A)-C(28)-H(28C)	109(2)	Cl(5)-C(31)-H(31B)	113.1(16)
H(28B)-C(28)-H(28C)	110(2)	Cl(4)-C(31)-H(31B)	107.9(16)
N(1)-C(29)-H(29A)	112.1(15)	H(31A)-C(31)-H(31B)	104(2)

Table 6. Anisotropic displacement parameters ($Å^2 x 10^4$) for 2 (CCDC 205652). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr(1)	129(2)	107(2)	105(2)	-7(2)	-13(1)	3(2)
Cl(1)	198(3)	192(3)	111(3)	-6(2)	-21(2)	-1(3)
Cl(2)	165(3)	136(3)	147(3)	4(2)	-4(2)	-15(2)
Cl(3)	150(3)	143(3)	209(3)	-33(2)	-4(2)	28(2)
P(1)	142(3)	116(3)	111(3)	3(2)	-13(2)	14(2)
P(2)	141(3)	114(3)	109(3)	4(2)	-17(2)	1(3)
O(1)	130(9)	106(8)	166(8)	-19(6)	-21(7)	-1(7)
O(2)	323(11)	268(10)	137(9)	46(7)	-48(8)	57(8)
O(3)	242(10)	330(11)	163(9)	-117(8)	17(7)	-69(8)
O(4)	118(9)	192(9)	183(9)	49(7)	-20(7)	4(7)
N(1)	146(11)	137(10)	82(10)	14(8)	-3(8)	10(8)
C(1)	185(15)	113(13)	291(16)	-7(11)	18(12)	15(11)
C(2)	129(13)	211(13)	107(12)	8(10)	-4(9)	29(10)
C(3)	147(13)	160(12)	80(11)	3(9)	-9(9)	12(10)
C(4)	195(14)	169(14)	171(13)	-14(10)	-3(10)	39(11)
C(5)	119(13)	335(16)	199(14)	-5(11)	10(11)	52(12)
C(6)	157(14)	271(15)	212(14)	-14(11)	-33(11)	-41(12)
C(7)	188(14)	177(13)	188(13)	-31(10)	0(10)	-2(11)
C(8)	147(13)	134(12)	167(12)	12(10)	38(10)	34(10)
C(9)	174(13)	165(13)	215(14)	14(11)	25(11)	24(10)
C(10)	202(14)	165(14)	346(16)	-39(12)	47(12)	2(11)
C(11)	277(16)	132(14)	470(19)	40(13)	60(13)	17(12)
C(12)	261(16)	264(16)	291(16)	149(13)	37(13)	71(12)
C(13)	189(13)	203(13)	206(13)	35(11)	10(11)	30(11)
C(14)	410(20)	430(20)	175(15)	76(14)	-75(14)	80(17)
C(15)	164(13)	119(12)	122(12)	48(9)	-25(10)	-22(10)
C(16)	201(14)	130(12)	152(13)	32(10)	-30(10)	6(10)
C(17)	153(14)	190(13)	221(14)	59(10)	-10(11)	-4(11)
C(18)	201(14)	198(14)	235(14)	64(11)	-96(11)	-65(11)
C(19)	291(15)	209(13)	131(13)	2(11)	-53(11)	-34(12)
C(20)	191(13)	164(12)	168(13)	33(10)	-21(10)	-19(10)
C(21)	350(20)	560(20)	269(17)	-231(15)	40(15)	-82(17)
C(22)	154(12)	109(12)	120(11)	11(9)	-3(9)	8(10)
C(23)	183(14)	140(12)	167(13)	5(10)	-37(10)	-6(11)
C(24)	234(15)	156(13)	199(14)	37(10)	-63(11)	38(11)
C(25)	292(15)	137(13)	149(13)	40(10)	-15(11)	-40(11)
C(26)	202(14)	167(13)	195(13)	18(10)	3(11)	-45(11)
C(27)	184(13)	121(12)	124(12)	-18(9)	-28(10)	15(10)
C(28)	171(14)	287(17)	277(16)	61(13)	36(12)	3(12)
C(29)	230(15)	192(14)	130(13)	12(11)	34(11)	49(11)
Cl(4)	349(4)	345(4)	271(4)	48(3)	80(3)	122(3)
Cl(5)	503(5)	328(4)	548(5)	135(4)	226(4)	104(4)
C(31)	317(18)	372(17)	192(16)	11(13)	43(13)	-3(14)

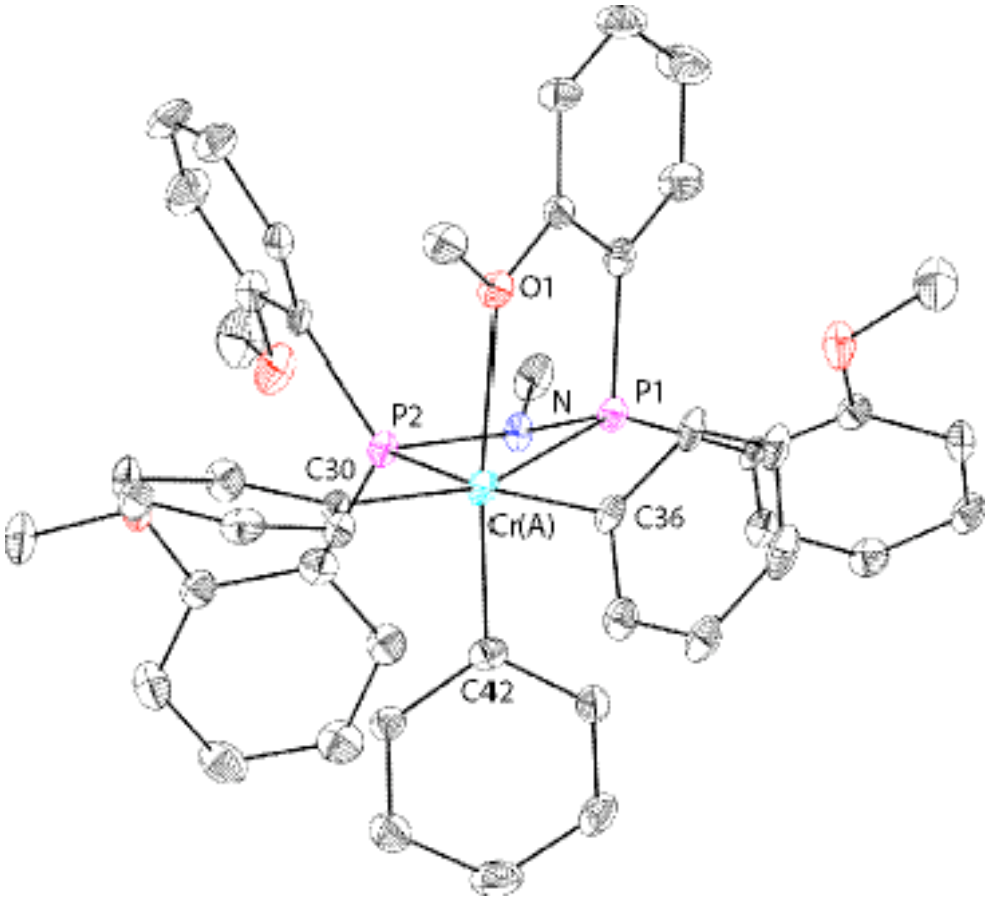


Figure 15. Structural drawing of **3** with thermal ellipsoids at the 50% probability level.

Table 7. Crystal data and structure refinement for 3 (CCDC 216617).

Empirical formula	$C_{47}H_{46}NO_4P_2Cr \cdot 3CH_2Cl_2$
Formula weight	1057.57
Crystallization Solvent	Dichloromethane/petroleum ether
Crystal Habit	Block
Crystal size	0.26 x 0.17 x 0.11 mm^3
Crystal color	Dark red

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoK□	
Data Collection Temperature	98(2) K	
□ range for 23120 reflections used in lattice determination	2.20 to 27.69°	
Unit cell dimensions	a = 15.1624(7) Å b = 15.4024(7) Å c = 22.7168(11) Å	□= 91.2320(10)° □= 94.4350(10)° □= 110.5250(10)°
Volume	4946.8(4) $Å^3$	
Z	4	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.420 Mg/m^3	
F(000)	2188	
□ range for data collection	1.41 to 28.46°	
Completeness to □ = 28.46°	91.7 %	
Index ranges	$-20 \le h \le 20$, $-20 \le k \le 20$, $-30 \le l \le 29$	
Data collection scan type	□ scans at 7 □ settings	
Reflections collected	102892	
Independent reflections	22906 [R_{int}= 0.0806]	
Absorption coefficient	0.665 mm^{-1}	
Absorption correction	None	
Max. and min. transmission (predicted)	0.9304 and 0.8461	

Table 7 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	22906 / 0 / 1138
Treatment of hydrogen atoms	Constrained
Goodness-of-fit on F^2	2.003
Final R indices [I>2□(I), 14122 reflections]	R1 = 0.0692, *w*R2 = 0.1163
R indices (all data)	R1 = 0.1196, *w*R2 = 0.1216
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/□^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000
Largest diff. peak and hole	2.556 and -1.427 e.Å^{-3}

Special Refinement Details

The crystals contain dichloromethane as solvent of crystallization. Each asymmetric unit contains six molecules of dichloromethane, four of which are occupied by distinct and ordered molecules (Cl 1-8 and C 1-4). These four were refined with anisotropic displacement parameters. The other two solvent sites are disordered and adjacent to each other. They are modeled by five molecules with partial occupancies (Cl 9-18 and C 5-9). Three of these five molecules (Cl 13-18 and C 7-9) were included in the structure factor calculations but neither the coordinates nor temperature factors were refined during least-squares. Hydrogen atoms were restrained to ride on the atoms they are bonded to. No other restraints were applied during refinement.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2□(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3 (CCDC 216617). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Cr(1)	7825(1)	8572(1)	709(1)	14(1)	1
P(1A)	7077(1)	9574(1)	1188(1)	14(1)	1
P(2A)	7502(1)	8284(1)	1835(1)	15(1)	1
O(1A)	9029(2)	9938(2)	1000(1)	15(1)	1
O(2A)	7017(2)	11087(2)	453(1)	21(1)	1
O(3A)	8011(2)	6763(2)	2332(1)	22(1)	1
O(4A)	7334(2)	8210(2)	3176(1)	23(1)	1
N(1A)	6824(2)	8973(2)	1810(1)	14(1)	1
C(1A)	9953(2)	10064(3)	799(2)	25(1)	1
C(2A)	8948(3)	10702(3)	1298(2)	16(1)	1
C(3A)	8043(3)	10635(3)	1421(2)	16(1)	1
C(4A)	7940(3)	11384(3)	1724(2)	26(1)	1
C(5A)	8698(3)	12175(3)	1895(2)	35(1)	1
C(6A)	9595(3)	12221(3)	1765(2)	29(1)	1
C(7A)	9724(3)	11491(3)	1464(2)	20(1)	1
C(8A)	6069(2)	9925(3)	1008(2)	13(1)	1
C(9A)	6157(3)	10681(3)	657(2)	16(1)	1
C(10A)	7203(3)	11946(3)	185(2)	32(1)	1
C(11A)	5392(3)	10953(3)	522(2)	18(1)	1
C(12A)	4524(3)	10466(3)	717(2)	19(1)	1
C(13A)	4421(3)	9701(3)	1047(2)	19(1)	1
C(14A)	5182(2)	9429(3)	1191(2)	17(1)	1
C(15A)	6705(3)	7179(3)	2048(2)	18(1)	1
C(16A)	7046(3)	6487(3)	2251(2)	18(1)	1
C(17A)	8396(3)	6051(3)	2431(2)	27(1)	1
C(18A)	6439(3)	5615(3)	2345(2)	24(1)	1
C(19A)	5473(3)	5403(3)	2239(2)	28(1)	1
C(20A)	5124(3)	6068(3)	2035(2)	25(1)	1
C(21A)	5742(3)	6947(3)	1941(2)	20(1)	1
C(22A)	8406(3)	8741(3)	2455(2)	16(1)	1
C(23A)	8245(3)	8651(3)	3054(2)	22(1)	1
C(24A)	7127(3)	8211(3)	3779(2)	34(1)	1
C(25A)	8999(3)	9008(3)	3484(2)	31(1)	1
C(26A)	9892(3)	9443(3)	3326(2)	35(1)	1
C(27A)	10063(3)	9549(3)	2741(2)	26(1)	1
C(28A)	9326(3)	9191(3)	2310(2)	19(1)	1
C(29A)	6567(3)	9343(3)	2347(2)	21(1)	1
C(30A)	8741(2)	7840(2)	589(2)	13(1)	1
C(31A)	9117(3)	7749(3)	59(2)	18(1)	1
C(32A)	9813(3)	7365(3)	10(2)	20(1)	1
C(33A)	10151(3)	7029(3)	504(2)	22(1)	1
C(34A)	9782(3)	7071(3)	1038(2)	22(1)	1
C(35A)	9101(3)	7478(3)	1077(2)	21(1)	1
C(36A)	7763(2)	9028(3)	-141(2)	14(1)	1
C(37A)	8088(2)	9975(3)	-269(2)	18(1)	1
C(38A)	8042(3)	10272(3)	-835(2)	21(1)	1
C(39A)	7667(3)	9637(3)	-1309(2)	24(1)	1

C(40A)	7338(3)	8697(3)	-1210(2)	22(1)	1
C(41A)	7383(3)	8412(3)	-636(2)	20(1)	1
C(42A)	6585(3)	7471(3)	560(2)	15(1)	1
C(43A)	6500(3)	6555(3)	682(2)	16(1)	1
C(44A)	5654(3)	5826(3)	619(2)	23(1)	1
C(45A)	4827(3)	5979(3)	421(2)	28(1)	1
C(46A)	4876(3)	6865(3)	286(2)	24(1)	1
C(47A)	5739(3)	7591(3)	355(2)	19(1)	1
Cr(2)	1515(1)	4732(1)	3865(1)	18(1)	1
P(1B)	3155(1)	5916(1)	3969(1)	18(1)	1
P(2B)	2091(1)	5590(1)	2908(1)	17(1)	1
O(1B)	1395(2)	6061(2)	4249(1)	21(1)	1
O(2B)	3968(2)	6235(2)	5187(1)	25(1)	1
O(3B)	748(2)	4989(2)	1850(1)	25(1)	1
O(4B)	2743(2)	6704(2)	1829(1)	25(1)	1
N(1B)	3224(2)	6092(2)	3235(1)	16(1)	1
C(1B)	486(3)	5970(3)	4460(2)	36(1)	1
C(2B)	2109(3)	6911(3)	4379(2)	21(1)	1
C(3B)	3023(3)	6956(3)	4281(2)	21(1)	1
C(4B)	3767(3)	7797(3)	4411(2)	24(1)	1
C(5B)	3611(3)	8575(3)	4626(2)	33(1)	1
C(6B)	2698(3)	8509(3)	4716(2)	34(1)	1
C(7B)	1952(3)	7689(3)	4599(2)	29(1)	1
C(8B)	4341(3)	5986(3)	4237(2)	18(1)	1
C(9B)	4630(3)	6147(3)	4834(2)	20(1)	1
C(10B)	4250(3)	6525(3)	5791(2)	32(1)	1
C(11B)	5529(3)	6188(3)	5043(2)	24(1)	1
C(12B)	6127(3)	6043(3)	4659(2)	26(1)	1
C(13B)	5837(3)	5849(3)	4068(2)	25(1)	1
C(14B)	4946(3)	5821(3)	3861(2)	22(1)	1
C(15B)	2181(3)	4921(3)	2266(2)	17(1)	1
C(16B)	1475(3)	4673(3)	1791(2)	19(1)	1
C(17B)	4(3)	4761(3)	1389(2)	27(1)	1
C(18B)	1538(3)	4144(3)	1304(2)	23(1)	1
C(19B)	2284(3)	3821(3)	1297(2)	26(1)	1
C(20B)	2958(3)	4027(3)	1767(2)	22(1)	1
C(21B)	2910(3)	4570(3)	2246(2)	18(1)	1
C(22B)	1800(3)	6559(3)	2623(2)	18(1)	1
C(23B)	2161(3)	7031(3)	2121(2)	22(1)	1
C(24B)	3034(3)	7067(3)	1282(2)	36(1)	1
C(25B)	1925(3)	7789(3)	1942(2)	30(1)	1
C(26B)	1333(3)	8079(3)	2266(2)	34(1)	1
C(27B)	971(3)	7626(3)	2759(2)	29(1)	1
C(28B)	1212(3)	6881(3)	2933(2)	21(1)	1
C(29B)	3912(3)	6945(3)	3023(2)	23(1)	1
C(30B)	65(3)	4145(3)	3609(2)	19(1)	1
C(31B)	-574(3)	3530(3)	3946(2)	30(1)	1
C(32B)	-1552(3)	3186(3)	3797(2)	32(1)	1
C(33B)	-1913(3)	3436(3)	3282(2)	27(1)	1
C(34B)	-1310(3)	4027(3)	2934(2)	23(1)	1
C(35B)	-353(3)	4384(3)	3095(2)	21(1)	1
C(36B)	1532(2)	4220(3)	4704(2)	18(1)	1
C(37B)	1807(3)	4785(3)	5225(2)	19(1)	1

C(38B)	1828(3)	4446(3)	5787(2)	21(1)	1
C(39B)	1554(3)	3502(3)	5849(2)	23(1)	1
C(40B)	1267(3)	2900(3)	5343(2)	23(1)	1
C(41B)	1274(3)	3264(3)	4791(2)	20(1)	1
C(42B)	1883(3)	3694(3)	3489(2)	18(1)	1
C(43B)	2783(3)	3639(3)	3619(2)	19(1)	1
C(44B)	3062(3)	2975(3)	3355(2)	24(1)	1
C(45B)	2455(3)	2315(3)	2953(2)	25(1)	1
C(46B)	1548(3)	2332(3)	2824(2)	29(1)	1
C(47B)	1279(3)	3007(3)	3083(2)	24(1)	1
Cl(1)	6394(1)	2780(1)	1849(1)	61(1)	1
Cl(2)	4737(1)	2689(1)	2430(1)	71(1)	1
C(1)	5199(4)	2222(5)	1883(3)	130(4)	1
Cl(3)	8613(1)	4531(1)	22(1)	36(1)	1
Cl(4)	7333(1)	4550(1)	902(1)	37(1)	1
C(2)	7905(3)	5117(3)	298(2)	28(1)	1
Cl(5)	4099(1)	9532(1)	2551(1)	86(1)	1
Cl(6)	2836(1)	10173(1)	3146(1)	91(1)	1
C(3)	3503(5)	9438(5)	3167(3)	96(3)	1
Cl(7)	3565(1)	1280(1)	4694(1)	79(1)	1
Cl(8)	1534(1)	675(1)	4738(1)	56(1)	1
C(4)	2553(4)	1538(3)	4517(2)	55(2)	1
Cl(9)	9001(1)	1035(1)	4340(1)	35(1)	0.602(3)
Cl(10)	8838(1)	1157(1)	3074(1)	35(1)	0.602(3)
C(5)	9571(5)	1432(5)	3723(3)	30(2)	0.602(3)
Cl(11)	4262(2)	8576(2)	6614(2)	50(1)	0.389(4)
Cl(12)	4103(2)	10233(2)	6090(2)	54(1)	0.389(4)
C(6)	3600(8)	9167(8)	6392(6)	41(3)	0.389(4)
Cl(13)	4336	8578	6283	70	0.197(4)
Cl(14)	4111	10223	6082	70	0.197(4)
C(7)	3440	9101	6181	70	0.197(4)
Cl(15)	2504	9206	6381	70	0.120(2)
Cl(16)	4837	9389	6268	70	0.120(2)
C(8)	3440	8857	6095	70	0.120(2)
Cl(17)	2510	9200	6380	70	0.230(3)
Cl(18)	9470	1217	4174	70	0.230(3)
C(9)	8690	1150	3519	70	0.230(3)

—

Table 9. Selected bond lengths [Å] and angles [°] for 3 (CCDC 216617).

Cr(1)-C(42A)	2.041(4)	C(42A)-Cr(1)-P(2A)	82.90(10)
Cr(1)-C(36A)	2.075(4)	C(36A)-Cr(1)-P(2A)	160.72(10)
Cr(1)-C(30A)	2.101(4)	C(30A)-Cr(1)-P(2A)	101.20(10)
Cr(1)-O(1A)	2.293(2)	O(1A)-Cr(1)-P(2A)	89.37(7)
Cr(1)-P(1A)	2.4897(11)	P(1A)-Cr(1)-P(2A)	63.67(3)
Cr(1)-P(2A)	2.6597(12)	C(42B)-Cr(2)-C(36B)	92.86(15)
Cr(2)-C(42B)	2.060(4)	C(42B)-Cr(2)-C(30B)	96.62(15)
Cr(2)-C(36B)	2.081(4)	C(36B)-Cr(2)-C(30B)	99.25(15)
Cr(2)-C(30B)	2.092(4)	C(42B)-Cr(2)-O(1B)	168.94(13)
Cr(2)-O(1B)	2.279(3)	C(36B)-Cr(2)-O(1B)	90.87(13)
Cr(2)-P(1B)	2.5044(12)	C(30B)-Cr(2)-O(1B)	93.04(12)
Cr(2)-P(2B)	2.6164(12)	C(42B)-Cr(2)-P(1B)	95.52(11)
C(42A)-Cr(1)-C(36A)	94.05(15)	C(36B)-Cr(2)-P(1B)	97.63(11)
C(42A)-Cr(1)-C(30A)	97.35(14)	C(30B)-Cr(2)-P(1B)	158.64(12)
C(36A)-Cr(1)-C(30A)	98.06(14)	O(1B)-Cr(2)-P(1B)	73.66(7)
C(42A)-Cr(1)-O(1A)	167.42(12)	C(42B)-Cr(2)-P(2B)	83.95(11)
C(36A)-Cr(1)-O(1A)	89.98(12)	C(36B)-Cr(2)-P(2B)	161.18(11)
C(30A)-Cr(1)-O(1A)	93.88(11)	C(30B)-Cr(2)-P(2B)	99.55(11)
C(42A)-Cr(1)-P(1A)	93.71(11)	O(1B)-Cr(2)-P(2B)	89.16(7)
C(36A)-Cr(1)-P(1A)	97.71(10)	P(1B)-Cr(2)-P(2B)	64.37(4)
C(30A)-Cr(1)-P(1A)	160.02(10)		
O(1A)-Cr(1)-P(1A)	73.92(7)		

Table 10. Bond lengths [Å] and angles [°] for 3 (CCDC 216617).

		C(32A)-C(33A)	1.382(5)
		C(33A)-C(34A)	1.385(5)
Cr(1)-C(42A)	2.041(4)	C(34A)-C(35A)	1.390(5)
Cr(1)-C(36A)	2.075(4)	C(36A)-C(41A)	1.401(5)
Cr(1)-C(30A)	2.101(4)	C(36A)-C(37A)	1.412(5)
Cr(1)-O(1A)	2.293(2)	C(37A)-C(38A)	1.380(5)
Cr(1)-P(1A)	2.4897(11)	C(38A)-C(39A)	1.381(5)
Cr(1)-P(2A)	2.6597(12)	C(39A)-C(40A)	1.387(5)
P(1A)-N(1A)	1.700(3)	C(40A)-C(41A)	1.390(5)
P(1A)-C(3A)	1.806(4)	C(42A)-C(47A)	1.405(5)
P(1A)-C(8A)	1.814(4)	C(42A)-C(43A)	1.407(5)
P(2A)-N(1A)	1.716(3)	C(43A)-C(44A)	1.372(5)
P(2A)-C(15A)	1.810(4)	C(44A)-C(45A)	1.398(5)
P(2A)-C(22A)	1.827(4)	C(45A)-C(46A)	1.382(5)
O(1A)-C(2A)	1.391(4)	C(46A)-C(47A)	1.386(5)
O(1A)-C(1A)	1.457(4)	Cr(2)-C(42B)	2.060(4)
O(2A)-C(9A)	1.356(4)	Cr(2)-C(36B)	2.081(4)
O(2A)-C(10A)	1.414(4)	Cr(2)-C(30B)	2.092(4)
O(3A)-C(16A)	1.369(4)	Cr(2)-O(1B)	2.279(3)
O(3A)-C(17A)	1.426(4)	Cr(2)-P(1B)	2.5044(12)
O(4A)-C(23A)	1.362(4)	Cr(2)-P(2B)	2.6164(12)
O(4A)-C(24A)	1.429(4)	P(1B)-N(1B)	1.702(3)
N(1A)-C(29A)	1.472(4)	P(1B)-C(8B)	1.819(4)
C(2A)-C(7A)	1.383(5)	P(1B)-C(3B)	1.819(4)
C(2A)-C(3A)	1.391(5)	P(2B)-N(1B)	1.718(3)
C(3A)-C(4A)	1.392(5)	P(2B)-C(15B)	1.807(4)
C(4A)-C(5A)	1.372(5)	P(2B)-C(22B)	1.816(4)
C(5A)-C(6A)	1.393(5)	O(1B)-C(2B)	1.383(4)
C(6A)-C(7A)	1.383(5)	O(1B)-C(1B)	1.454(4)
C(8A)-C(9A)	1.398(5)	O(2B)-C(9B)	1.372(4)
C(8A)-C(14A)	1.395(5)	O(2B)-C(10B)	1.419(4)
C(9A)-C(11A)	1.381(5)	O(3B)-C(16B)	1.367(4)
C(11A)-C(12A)	1.380(5)	O(3B)-C(17B)	1.421(4)
C(12A)-C(13A)	1.380(5)	O(4B)-C(23B)	1.365(4)
C(13A)-C(14A)	1.378(5)	O(4B)-C(24B)	1.412(4)
C(15A)-C(21A)	1.376(5)	N(1B)-C(29B)	1.479(5)
C(15A)-C(16A)	1.409(5)	C(2B)-C(7B)	1.391(5)
C(16A)-C(18A)	1.369(5)	C(2B)-C(3B)	1.398(5)
C(18A)-C(19A)	1.384(5)	C(3B)-C(4B)	1.395(5)
C(19A)-C(20A)	1.380(5)	C(4B)-C(5B)	1.386(5)
C(20A)-C(21A)	1.382(5)	C(5B)-C(6B)	1.384(6)
C(22A)-C(28A)	1.393(5)	C(6B)-C(7B)	1.372(6)
C(22A)-C(23A)	1.402(5)	C(8B)-C(9B)	1.382(5)
C(23A)-C(25A)	1.388(5)	C(8B)-C(14B)	1.383(5)
C(25A)-C(26A)	1.364(6)	C(9B)-C(11B)	1.387(5)
C(26A)-C(27A)	1.377(6)	C(11B)-C(12B)	1.373(5)
C(27A)-C(28A)	1.373(5)	C(12B)-C(13B)	1.374(5)
C(30A)-C(31A)	1.396(5)	C(13B)-C(14B)	1.381(5)
C(30A)-C(35A)	1.410(5)	C(15B)-C(21B)	1.393(5)
C(31A)-C(32A)	1.389(5)	C(15B)-C(16B)	1.406(5)

C(16B)-C(18B)	1.389(5)
C(18B)-C(19B)	1.387(5)
C(19B)-C(20B)	1.368(5)
C(20B)-C(21B)	1.381(5)
C(22B)-C(23B)	1.408(5)
C(22B)-C(28B)	1.388(5)
C(23B)-C(25B)	1.395(5)
C(25B)-C(26B)	1.384(6)
C(26B)-C(27B)	1.379(6)
C(27B)-C(28B)	1.377(5)
C(30B)-C(31B)	1.388(5)
C(30B)-C(35B)	1.404(5)
C(31B)-C(32B)	1.399(5)
C(32B)-C(33B)	1.372(5)
C(33B)-C(34B)	1.359(5)
C(34B)-C(35B)	1.375(5)
C(36B)-C(37B)	1.399(5)
C(36B)-C(41B)	1.408(5)
C(37B)-C(38B)	1.392(5)
C(38B)-C(39B)	1.379(5)
C(39B)-C(40B)	1.400(5)
C(40B)-C(41B)	1.383(5)
C(42B)-C(47B)	1.400(5)
C(42B)-C(43B)	1.404(5)
C(43B)-C(44B)	1.378(5)
C(44B)-C(45B)	1.374(5)
C(45B)-C(46B)	1.392(5)
C(46B)-C(47B)	1.378(5)
Cl(1)-C(1)	1.721(6)
Cl(2)-C(1)	1.733(5)
Cl(3)-C(2)	1.767(4)
Cl(4)-C(2)	1.762(4)
Cl(5)-C(3)	1.706(6)
Cl(6)-C(3)	1.761(5)
Cl(7)-C(4)	1.737(5)
Cl(8)-C(4)	1.764(5)
Cl(9)-C(5)	1.715(7)
Cl(10)-C(5)	1.726(7)
Cl(11)-C(6)	1.634(12)
Cl(12)-C(6)	1.731(12)
Cl(13)-C(7)	1.8092
Cl(14)-C(7)	1.7016
Cl(15)-C(8)	1.8406
Cl(16)-C(8)	1.9882
Cl(17)-C(9)#1	1.7424
Cl(18)-C(9)	1.8052
C(9)-Cl(17)#1	1.7424
C(42A)-Cr(1)-C(36A)	94.05(15)
C(42A)-Cr(1)-C(30A)	97.35(14)
C(36A)-Cr(1)-C(30A)	98.06(14)
C(42A)-Cr(1)-O(1A)	167.42(12)
C(36A)-Cr(1)-O(1A)	89.98(12)
C(30A)-Cr(1)-O(1A)	93.88(11)
C(42A)-Cr(1)-P(1A)	93.71(11)
C(36A)-Cr(1)-P(1A)	97.71(10)
C(30A)-Cr(1)-P(1A)	160.02(10)
O(1A)-Cr(1)-P(1A)	73.92(7)
C(42A)-Cr(1)-P(2A)	82.90(10)
C(36A)-Cr(1)-P(2A)	160.72(10)
C(30A)-Cr(1)-P(2A)	101.20(10)
O(1A)-Cr(1)-P(2A)	89.37(7)
P(1A)-Cr(1)-P(2A)	63.67(3)
N(1A)-P(1A)-C(3A)	105.38(16)
N(1A)-P(1A)-C(8A)	104.71(16)
C(3A)-P(1A)-C(8A)	105.16(17)
N(1A)-P(1A)-Cr(1)	97.02(11)
C(3A)-P(1A)-Cr(1)	104.99(12)
C(8A)-P(1A)-Cr(1)	136.20(12)
N(1A)-P(2A)-C(15A)	103.74(17)
N(1A)-P(2A)-C(22A)	106.92(16)
C(15A)-P(2A)-C(22A)	106.40(18)
N(1A)-P(2A)-Cr(1)	90.67(11)
C(15A)-P(2A)-Cr(1)	120.71(13)
C(22A)-P(2A)-Cr(1)	123.86(13)
C(2A)-O(1A)-C(1A)	116.0(3)
C(2A)-O(1A)-Cr(1)	126.6(2)
C(1A)-O(1A)-Cr(1)	117.0(2)
C(9A)-O(2A)-C(10A)	118.2(3)
C(16A)-O(3A)-C(17A)	116.6(3)
C(23A)-O(4A)-C(24A)	117.9(3)
C(29A)-N(1A)-P(1A)	123.6(3)
C(29A)-N(1A)-P(2A)	122.4(2)
P(1A)-N(1A)-P(2A)	105.52(16)
C(7A)-C(2A)-C(3A)	121.3(4)
C(7A)-C(2A)-O(1A)	122.2(3)
C(3A)-C(2A)-O(1A)	116.6(3)
C(4A)-C(3A)-C(2A)	118.0(4)
C(4A)-C(3A)-P(1A)	124.1(3)
C(2A)-C(3A)-P(1A)	117.9(3)
C(3A)-C(4A)-C(5A)	122.0(4)
C(6A)-C(5A)-C(4A)	118.7(4)
C(7A)-C(6A)-C(5A)	120.9(4)
C(6A)-C(7A)-C(2A)	119.1(4)
C(9A)-C(8A)-C(14A)	118.4(3)
C(9A)-C(8A)-P(1A)	120.3(3)
C(14A)-C(8A)-P(1A)	121.3(3)
O(2A)-C(9A)-C(8A)	115.6(3)
O(2A)-C(9A)-C(11A)	124.0(3)
C(8A)-C(9A)-C(11A)	120.4(3)
C(9A)-C(11A)-C(12A)	120.4(4)
C(13A)-C(12A)-C(11A)	119.6(4)
C(14A)-C(13A)-C(12A)	120.5(4)
C(13A)-C(14A)-C(8A)	120.6(4)
C(21A)-C(15A)-C(16A)	118.0(4)
C(21A)-C(15A)-P(2A)	120.3(3)
C(16A)-C(15A)-P(2A)	121.2(3)
O(3A)-C(16A)-C(18A)	124.4(4)

O(3A)-C(16A)-C(15A)	114.5(3)	P(1B)-Cr(2)-P(2B)	64.37(4)
C(18A)-C(16A)-C(15A)	121.0(4)	N(1B)-P(1B)-C(8B)	103.94(17)
C(19A)-C(18A)-C(16A)	119.8(4)	N(1B)-P(1B)-C(3B)	104.72(17)
C(20A)-C(19A)-C(18A)	120.1(4)	C(8B)-P(1B)-C(3B)	105.26(18)
C(19A)-C(20A)-C(21A)	119.8(4)	N(1B)-P(1B)-Cr(2)	95.94(11)
C(15A)-C(21A)-C(20A)	121.3(4)	C(8B)-P(1B)-Cr(2)	138.16(13)
C(28A)-C(22A)-C(23A)	118.5(4)	C(3B)-P(1B)-Cr(2)	104.66(13)
C(28A)-C(22A)-P(2A)	116.3(3)	N(1B)-P(2B)-C(15B)	105.58(16)
C(23A)-C(22A)-P(2A)	125.2(3)	N(1B)-P(2B)-C(22B)	104.19(16)
O(4A)-C(23A)-C(25A)	123.8(4)	C(15B)-P(2B)-C(22B)	105.87(18)
O(4A)-C(23A)-C(22A)	116.6(3)	N(1B)-P(2B)-Cr(2)	91.62(11)
C(25A)-C(23A)-C(22A)	119.6(4)	C(15B)-P(2B)-Cr(2)	119.05(13)
C(23A)-C(25A)-C(26A)	120.3(4)	C(22B)-P(2B)-Cr(2)	126.03(14)
C(27A)-C(26A)-C(25A)	120.9(4)	C(2B)-O(1B)-C(1B)	115.6(3)
C(26A)-C(27A)-C(28A)	119.4(4)	C(2B)-O(1B)-Cr(2)	127.9(2)
C(27A)-C(28A)-C(22A)	121.2(4)	C(1B)-O(1B)-Cr(2)	115.8(2)
C(31A)-C(30A)-C(35A)	114.6(3)	C(9B)-O(2B)-C(10B)	118.7(3)
C(31A)-C(30A)-Cr(1)	125.0(3)	C(16B)-O(3B)-C(17B)	118.4(3)
C(35A)-C(30A)-Cr(1)	120.1(3)	C(23B)-O(4B)-C(24B)	119.3(3)
C(30A)-C(31A)-C(32A)	123.7(4)	C(29B)-N(1B)-P(1B)	121.3(2)
C(33A)-C(32A)-C(31A)	119.5(4)	C(29B)-N(1B)-P(2B)	122.6(2)
C(32A)-C(33A)-C(34A)	119.5(4)	P(1B)-N(1B)-P(2B)	105.92(17)
C(35A)-C(34A)-C(33A)	119.8(4)	C(7B)-C(2B)-O(1B)	123.2(4)
C(34A)-C(35A)-C(30A)	122.9(4)	C(7B)-C(2B)-C(3B)	120.5(4)
C(41A)-C(36A)-C(37A)	114.6(4)	O(1B)-C(2B)-C(3B)	116.3(4)
C(41A)-C(36A)-Cr(1)	122.2(3)	C(4B)-C(3B)-C(2B)	118.3(4)
C(37A)-C(36A)-Cr(1)	123.1(3)	C(4B)-C(3B)-P(1B)	124.3(3)
C(38A)-C(37A)-C(36A)	122.7(4)	C(2B)-C(3B)-P(1B)	117.4(3)
C(39A)-C(38A)-C(37A)	120.5(4)	C(3B)-C(4B)-C(5B)	121.3(4)
C(38A)-C(39A)-C(40A)	119.2(4)	C(6B)-C(5B)-C(4B)	119.0(4)
C(39A)-C(40A)-C(41A)	119.4(4)	C(5B)-C(6B)-C(7B)	121.1(4)
C(40A)-C(41A)-C(36A)	123.5(4)	C(6B)-C(7B)-C(2B)	119.8(4)
C(47A)-C(42A)-C(43A)	115.2(3)	C(9B)-C(8B)-C(14B)	118.7(4)
C(47A)-C(42A)-Cr(1)	121.6(3)	C(9B)-C(8B)-P(1B)	119.9(3)
C(43A)-C(42A)-Cr(1)	123.1(3)	C(14B)-C(8B)-P(1B)	121.3(3)
C(44A)-C(43A)-C(42A)	123.0(4)	O(2B)-C(9B)-C(8B)	115.5(3)
C(43A)-C(44A)-C(45A)	119.8(4)	O(2B)-C(9B)-C(11B)	124.3(4)
C(44A)-C(45A)-C(46A)	119.3(4)	C(8B)-C(9B)-C(11B)	120.1(4)
C(47A)-C(46A)-C(45A)	119.8(4)	C(12B)-C(11B)-C(9B)	120.2(4)
C(46A)-C(47A)-C(42A)	122.8(4)	C(11B)-C(12B)-C(13B)	120.3(4)
C(42B)-Cr(2)-C(36B)	92.86(15)	C(14B)-C(13B)-C(12B)	119.3(4)
C(42B)-Cr(2)-C(30B)	96.62(15)	C(13B)-C(14B)-C(8B)	121.2(4)
C(36B)-Cr(2)-C(30B)	99.25(15)	C(21B)-C(15B)-C(16B)	117.6(4)
C(42B)-Cr(2)-O(1B)	168.94(13)	C(21B)-C(15B)-P(2B)	121.2(3)
C(36B)-Cr(2)-O(1B)	90.87(13)	C(16B)-C(15B)-P(2B)	121.0(3)
C(30B)-Cr(2)-O(1B)	93.04(12)	O(3B)-C(16B)-C(18B)	124.1(4)
C(42B)-Cr(2)-P(1B)	95.52(11)	O(3B)-C(16B)-C(15B)	115.1(3)
C(36B)-Cr(2)-P(1B)	97.63(11)	C(18B)-C(16B)-C(15B)	120.8(4)
C(30B)-Cr(2)-P(1B)	158.64(12)	C(16B)-C(18B)-C(19B)	119.7(4)
O(1B)-Cr(2)-P(1B)	73.66(7)	C(20B)-C(19B)-C(18B)	120.2(4)
C(42B)-Cr(2)-P(2B)	83.95(11)	C(19B)-C(20B)-C(21B)	120.4(4)
C(36B)-Cr(2)-P(2B)	161.18(11)	C(15B)-C(21B)-C(20B)	121.3(4)
C(30B)-Cr(2)-P(2B)	99.55(11)	C(23B)-C(22B)-C(28B)	117.5(4)
O(1B)-Cr(2)-P(2B)	89.16(7)	C(23B)-C(22B)-P(2B)	124.4(3)

C(28B)-C(22B)-P(2B)	118.1(3)	C(38B)-C(39B)-C(40B)	119.3(4)
O(4B)-C(23B)-C(22B)	116.2(4)	C(39B)-C(40B)-C(41B)	119.5(4)
O(4B)-C(23B)-C(25B)	122.9(4)	C(40B)-C(41B)-C(36B)	123.4(4)
C(22B)-C(23B)-C(25B)	120.8(4)	C(47B)-C(42B)-C(43B)	115.0(4)
C(26B)-C(25B)-C(23B)	119.2(4)	C(47B)-C(42B)-Cr(2)	123.5(3)
C(25B)-C(26B)-C(27B)	120.9(4)	C(43B)-C(42B)-Cr(2)	121.5(3)
C(28B)-C(27B)-C(26B)	119.3(4)	C(44B)-C(43B)-C(42B)	122.7(4)
C(27B)-C(28B)-C(22B)	122.2(4)	C(43B)-C(44B)-C(45B)	120.9(4)
C(31B)-C(30B)-C(35B)	114.0(4)	C(44B)-C(45B)-C(46B)	118.1(4)
C(31B)-C(30B)-Cr(2)	123.3(3)	C(47B)-C(46B)-C(45B)	120.7(4)
C(35B)-C(30B)-Cr(2)	122.6(3)	C(46B)-C(47B)-C(42B)	122.6(4)
C(30B)-C(31B)-C(32B)	123.4(4)	Cl(1)-C(1)-Cl(2)	113.6(3)
C(33B)-C(32B)-C(31B)	119.4(4)	Cl(4)-C(2)-Cl(3)	110.5(2)
C(34B)-C(33B)-C(32B)	119.0(4)	Cl(5)-C(3)-Cl(6)	110.7(3)
C(33B)-C(34B)-C(35B)	121.0(4)	Cl(8)-C(4)-Cl(7)	111.8(3)
C(34B)-C(35B)-C(30B)	123.0(4)	Cl(9)-C(5)-Cl(10)	113.9(4)
C(37B)-C(36B)-C(41B)	114.5(4)	Cl(12)-C(6)-Cl(11)	120.1(7)
C(37B)-C(36B)-Cr(2)	123.5(3)	Cl(14)-C(7)-Cl(13)	101.340(4)
C(41B)-C(36B)-Cr(2)	122.0(3)	Cl(15)-C(8)-Cl(16)	130.592(3)
C(38B)-C(37B)-C(36B)	123.7(4)	Cl(17)#1-C(9)-Cl(18)	115.854(3)
C(39B)-C(38B)-C(37B)	119.6(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table 11. Anisotropic displacement parameters ($Å^2 x 10^4$) for 3 (CCDC 216617). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr(1)	110(3)	172(4)	146(3)	18(3)	14(3)	77(3)
P(1A)	112(5)	168(6)	156(6)	16(5)	15(4)	70(4)
P(2A)	126(5)	172(6)	160(6)	26(5)	9(4)	73(5)
O(1A)	101(13)	194(16)	172(15)	18(12)	36(11)	66(12)
O(2A)	156(15)	233(17)	261(17)	119(13)	68(13)	95(13)
O(3A)	181(15)	231(17)	279(17)	93(13)	36(13)	119(13)
O(4A)	220(16)	345(18)	139(15)	68(13)	31(12)	109(14)
N(1A)	170(17)	188(19)	106(17)	23(14)	29(14)	110(15)
C(1A)	110(20)	240(30)	390(30)	-10(20)	76(19)	55(19)
C(2A)	190(20)	150(20)	130(20)	1(17)	-18(17)	71(18)
C(3A)	160(20)	200(20)	140(20)	23(18)	24(17)	97(18)
C(4A)	180(20)	260(30)	340(30)	-80(20)	10(20)	90(20)
C(5A)	290(30)	240(30)	520(30)	-150(20)	20(20)	90(20)
C(6A)	170(20)	210(30)	410(30)	-50(20)	0(20)	-10(20)
C(7A)	120(20)	210(20)	240(20)	-9(19)	32(18)	15(18)
C(8A)	93(19)	190(20)	140(20)	4(17)	-21(16)	91(17)
C(9A)	110(20)	200(20)	160(20)	-3(18)	24(17)	69(18)
C(10A)	210(20)	340(30)	410(30)	170(20)	100(20)	90(20)
C(11A)	200(20)	190(20)	190(20)	35(18)	7(18)	119(19)
C(12A)	130(20)	270(30)	220(20)	-15(19)	-3(18)	123(19)
C(13A)	120(20)	230(20)	230(20)	8(19)	48(18)	61(18)
C(14A)	160(20)	200(20)	160(20)	19(18)	11(17)	81(18)
C(15A)	210(20)	200(20)	130(20)	-11(18)	32(17)	72(19)
C(16A)	170(20)	220(20)	160(20)	-12(18)	10(17)	94(19)
C(17A)	270(20)	320(30)	300(30)	80(20)	10(20)	190(20)
C(18A)	250(20)	230(30)	290(30)	80(20)	90(20)	120(20)
C(19A)	250(20)	190(20)	370(30)	50(20)	110(20)	40(20)
C(20A)	180(20)	260(30)	310(30)	20(20)	80(20)	60(20)
C(21A)	170(20)	210(20)	220(20)	14(19)	48(18)	84(19)
C(22A)	170(20)	170(20)	180(20)	4(18)	-35(17)	108(18)
C(23A)	240(20)	230(20)	220(20)	50(20)	-10(19)	120(20)
C(24A)	410(30)	460(30)	190(30)	70(20)	70(20)	200(30)
C(25A)	330(30)	380(30)	190(20)	50(20)	-50(20)	110(20)
C(26A)	330(30)	350(30)	270(30)	-10(20)	-190(20)	60(20)
C(27A)	160(20)	270(30)	320(30)	30(20)	-30(20)	50(20)
C(28A)	180(20)	160(20)	240(20)	32(18)	-17(18)	78(18)
C(29A)	210(20)	330(30)	130(20)	-20(19)	8(18)	140(20)
C(30A)	100(19)	130(20)	140(20)	23(17)	-7(16)	38(16)
C(31A)	190(20)	180(20)	180(20)	12(18)	-34(18)	76(18)
C(32A)	140(20)	230(20)	230(20)	-49(19)	48(18)	56(19)
C(33A)	120(20)	230(20)	340(30)	0(20)	13(19)	90(19)
C(34A)	220(20)	240(30)	250(30)	50(20)	-9(19)	150(20)
C(35A)	180(20)	230(20)	240(20)	14(19)	68(18)	100(19)
C(36A)	78(19)	230(20)	160(20)	15(18)	30(16)	103(17)
C(37A)	120(20)	290(30)	180(20)	42(19)	16(17)	132(19)
C(38A)	140(20)	290(30)	230(20)	100(20)	31(18)	130(19)
C(39A)	170(20)	440(30)	180(20)	110(20)	65(18)	200(20)

C(40A)	160(20)	370(30)	180(20)	0(20)	12(18)	160(20)
C(41A)	180(20)	250(20)	220(20)	10(20)	23(18)	134(19)
C(42A)	150(20)	180(20)	110(20)	-27(17)	19(16)	53(18)
C(43A)	130(20)	180(20)	180(20)	-28(18)	2(17)	66(18)
C(44A)	230(20)	200(20)	280(30)	-3(19)	42(19)	80(20)
C(45A)	170(20)	250(30)	360(30)	-50(20)	0(20)	20(20)
C(46A)	160(20)	330(30)	270(30)	-40(20)	-32(19)	140(20)
C(47A)	210(20)	190(20)	180(20)	1(18)	-2(18)	94(19)
Cr(2)	138(3)	262(4)	147(4)	25(3)	7(3)	90(3)
P(1B)	154(5)	240(6)	145(6)	3(5)	-5(4)	90(5)
P(2B)	142(5)	230(6)	148(6)	19(5)	-3(4)	79(5)
O(1B)	141(14)	303(18)	206(16)	50(13)	46(12)	111(13)
O(2B)	228(16)	420(20)	137(16)	25(14)	-8(13)	156(15)
O(3B)	162(15)	417(19)	180(16)	-59(14)	-61(12)	146(14)
O(4B)	295(17)	289(18)	205(17)	105(14)	85(13)	125(14)
N(1B)	149(17)	203(19)	110(17)	3(14)	-10(14)	58(15)
C(1B)	210(20)	450(30)	450(30)	10(20)	100(20)	160(20)
C(2B)	270(20)	240(30)	150(20)	17(19)	-10(19)	110(20)
C(3B)	250(20)	270(30)	130(20)	34(19)	4(18)	130(20)
C(4B)	250(20)	250(30)	180(20)	-62(19)	-39(19)	70(20)
C(5B)	380(30)	270(30)	290(30)	-50(20)	-40(20)	100(20)
C(6B)	510(30)	240(30)	280(30)	-50(20)	20(20)	180(20)
C(7B)	350(30)	370(30)	250(30)	40(20)	70(20)	230(20)
C(8B)	170(20)	180(20)	170(20)	-10(18)	-38(17)	57(18)
C(9B)	210(20)	210(20)	190(20)	35(19)	22(18)	76(19)
C(10B)	290(30)	510(30)	170(20)	0(20)	10(20)	170(20)
C(11B)	200(20)	280(30)	210(20)	40(20)	-34(19)	60(20)
C(12B)	110(20)	310(30)	340(30)	60(20)	-13(19)	48(19)
C(13B)	160(20)	320(30)	270(30)	50(20)	36(19)	100(20)
C(14B)	210(20)	240(20)	200(20)	16(19)	-14(19)	78(19)
C(15B)	160(20)	220(20)	130(20)	24(18)	21(17)	67(18)
C(16B)	140(20)	210(20)	200(20)	30(19)	33(18)	47(18)
C(17B)	190(20)	340(30)	280(30)	-10(20)	-75(19)	100(20)
C(18B)	210(20)	240(30)	190(20)	0(19)	-29(18)	38(19)
C(19B)	290(30)	240(30)	240(30)	-60(20)	40(20)	80(20)
C(20B)	170(20)	210(20)	270(30)	-10(20)	34(19)	82(19)
C(21B)	130(20)	200(20)	190(20)	51(18)	3(17)	43(18)
C(22B)	150(20)	180(20)	190(20)	23(18)	-32(17)	57(18)
C(23B)	190(20)	260(30)	210(20)	20(20)	-27(19)	80(20)
C(24B)	370(30)	490(30)	220(30)	150(20)	90(20)	160(20)
C(25B)	270(30)	370(30)	260(30)	110(20)	-20(20)	110(20)
C(26B)	270(30)	320(30)	490(30)	90(20)	-30(20)	200(20)
C(27B)	250(20)	320(30)	350(30)	30(20)	20(20)	160(20)
C(28B)	180(20)	250(30)	210(20)	34(19)	-32(18)	91(19)
C(29B)	170(20)	260(30)	230(20)	10(20)	-11(18)	59(19)
C(30B)	160(20)	270(30)	160(20)	5(19)	49(17)	118(19)
C(31B)	190(20)	460(30)	260(30)	90(20)	0(20)	110(20)
C(32B)	190(20)	490(30)	240(30)	120(20)	40(20)	60(20)
C(33B)	150(20)	370(30)	270(30)	-30(20)	-30(19)	100(20)
C(34B)	250(20)	250(30)	230(20)	-30(20)	-44(19)	150(20)
C(35B)	200(20)	220(20)	230(20)	-1(19)	7(18)	108(19)
C(36B)	110(20)	300(30)	170(20)	33(19)	48(17)	108(19)
C(37B)	190(20)	240(20)	180(20)	33(19)	45(18)	122(19)

C(38B)	200(20)	280(30)	160(20)	-13(19)	26(18)	100(20)
C(39B)	180(20)	390(30)	170(20)	100(20)	62(18)	170(20)
C(40B)	160(20)	240(30)	270(30)	40(20)	18(19)	73(19)
C(41B)	160(20)	310(30)	150(20)	-18(19)	-22(17)	100(20)
C(42B)	160(20)	270(30)	120(20)	23(18)	28(17)	72(19)
C(43B)	160(20)	230(20)	150(20)	20(18)	-31(17)	67(19)
C(44B)	190(20)	340(30)	210(20)	0(20)	18(19)	120(20)
C(45B)	290(20)	220(30)	260(30)	0(20)	40(20)	120(20)
C(46B)	240(20)	290(30)	270(30)	-70(20)	-30(20)	20(20)
C(47B)	140(20)	320(30)	230(20)	-30(20)	17(18)	60(20)
Cl(1)	446(8)	744(11)	684(10)	2(8)	113(7)	264(8)
Cl(2)	543(9)	814(12)	773(12)	-192(9)	209(8)	219(9)
C(1)	450(40)	1740(80)	1500(70)	-1140(60)	250(40)	150(50)
Cl(3)	455(7)	402(7)	314(7)	3(6)	62(6)	254(6)
Cl(4)	309(6)	395(7)	438(8)	49(6)	103(6)	147(6)
C(2)	190(20)	270(30)	430(30)	60(20)	40(20)	130(20)
Cl(5)	643(11)	1161(15)	765(12)	68(11)	280(9)	260(11)
Cl(6)	1023(14)	894(14)	932(14)	-94(11)	-132(11)	528(12)
C(3)	1590(70)	1420(70)	530(40)	300(40)	290(40)	1280(60)
Cl(7)	719(11)	495(10)	1169(15)	39(10)	313(10)	200(9)
Cl(8)	611(9)	496(9)	467(9)	-129(7)	1(7)	99(7)
C(4)	800(40)	450(40)	360(30)	160(30)	60(30)	160(30)

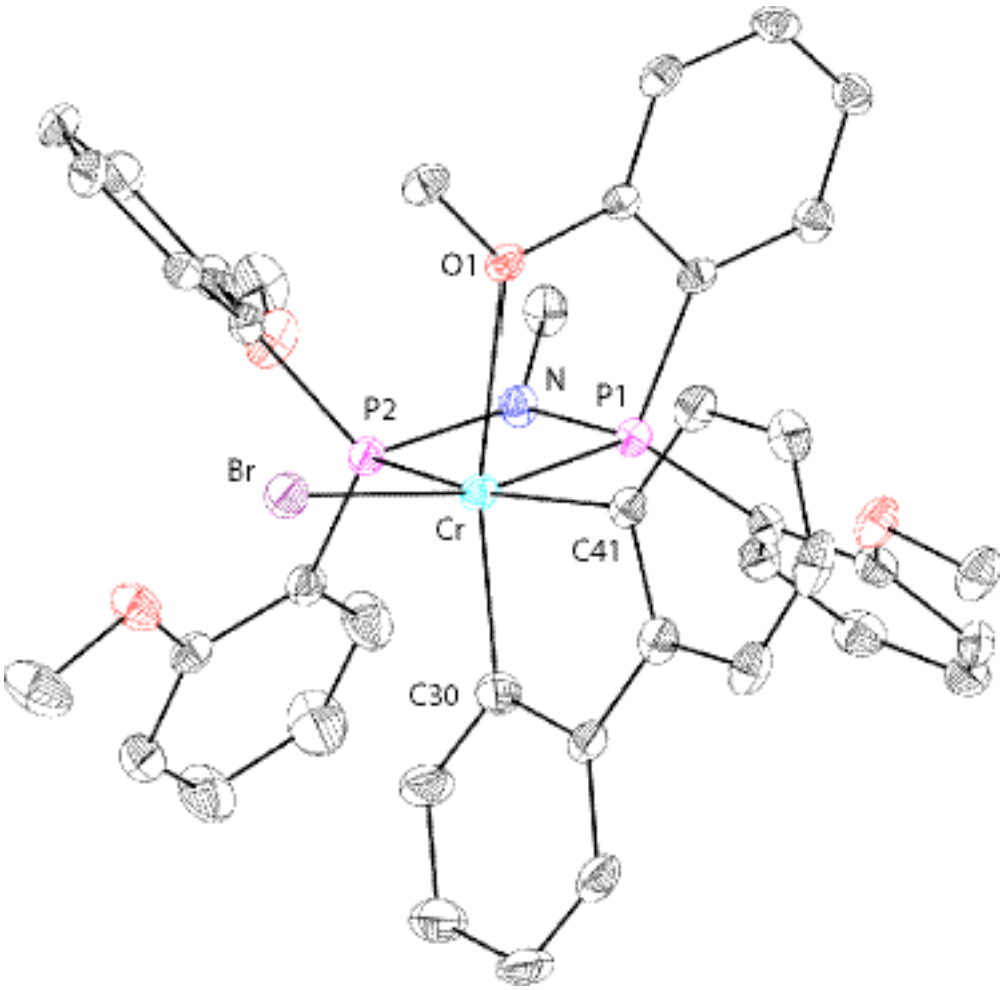


Figure 16. Structural drawing of **4** with thermal ellipsoids at the 50% probability level.

Table 12. Crystal data and structure refinement for 4 (CCDC 208405).

Empirical formula	$C_{41}H_{39}NO_4P_2BrCr \cdot CH_2Cl_2$
Formula weight	888.51
Crystallization Solvent	Dichloromethane/petroleum ether
Crystal Habit	Fragment
Crystal size	0.43 x 0.19 x 0.03 mm^3
Crystal color	Green

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoK□	
Data Collection Temperature	98(2) K	
□ range for 16724 reflections used in lattice determination	2.21 to 27.85°	
Unit cell dimensions	a = 9.9167(6) Å b = 11.9935(8) Å c = 17.9725(11) Å	□= 77.3710(10)° □= 76.3280(10)° □= 70.6700(10)°
Volume	1936.8(2) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.524 Mg/m^3	
F(000)	910	
□ range for data collection	1.82 to 28.29°	
Completeness to □ = 28.29°	91.9 %	
Index ranges	$-12 \le h \le 13$, $-15 \le k \le 15$, $-23 \le l \le 23$	
Data collection scan type	□ scans at 7 □ settings	
Reflections collected	44019	
Independent reflections	8816 [R_{int}= 0.0683]	
Absorption coefficient	1.592 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9538 and 0.5477	

Table 12 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8816 / 0 / 511
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.731
Final R indices [I>2□(I), 6545 reflections]	R1 = 0.0416, *w*R2 = 0.0744
R indices (all data)	R1 = 0.0657, *w*R2 = 0.0765
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/□^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	0.820 and -0.599 e.Å^{-3}

Special Refinement Details

The crystals contain dichloromethane as a solvent of crystallization. There is one solvent site per asymmetric unit. The dichloromethane in this site is disordered between two orientations with relative occupancies of approximately 80:20 (see Table 2). The non-hydrogen atoms of both orientations were refined anisotropically. All hydrogen atoms in the structure were restrained to ride on the atoms to which they are bonded.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2□(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 4 (CCDC 208405). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Cr(1)	8942(1)	8259(1)	1854(1)	15(1)	1
Br(1)	9932(1)	9902(1)	1865(1)	22(1)	1
P(1)	7332(1)	7132(1)	1821(1)	15(1)	1
P(2)	6368(1)	8830(1)	2778(1)	15(1)	1
O(1)	7653(2)	9266(2)	850(1)	15(1)	1
O(2)	9422(2)	5153(2)	1140(1)	22(1)	1
O(3)	7145(2)	9783(2)	3856(1)	24(1)	1
O(4)	3154(2)	9653(2)	3397(1)	26(1)	1
N(1)	5833(2)	7901(2)	2386(1)	16(1)	1
C(1)	6911(3)	7580(2)	854(2)	14(1)	1
C(2)	6385(3)	6943(3)	490(2)	18(1)	1
C(3)	6068(3)	7381(3)	-250(2)	19(1)	1
C(4)	6306(3)	8452(3)	-631(2)	20(1)	1
C(5)	6826(3)	9103(2)	-290(2)	17(1)	1
C(6)	7123(3)	8668(2)	455(2)	13(1)	1
C(7)	7850(3)	10396(2)	434(2)	19(1)	1
C(8)	7384(3)	5576(2)	2101(2)	18(1)	1
C(9)	6374(3)	5205(3)	2700(2)	21(1)	1
C(10)	6494(3)	3998(3)	2933(2)	25(1)	1
C(11)	7665(3)	3148(3)	2569(2)	25(1)	1
C(12)	8681(3)	3484(3)	1981(2)	22(1)	1
C(13)	8533(3)	4705(3)	1734(2)	19(1)	1
C(14)	10711(3)	4314(3)	799(2)	26(1)	1
C(15)	5986(3)	8402(2)	3830(2)	19(1)	1
C(16)	5264(4)	7569(3)	4204(2)	33(1)	1
C(17)	5071(4)	7266(3)	5004(2)	40(1)	1
C(18)	5647(4)	7776(3)	5432(2)	37(1)	1
C(19)	6353(3)	8624(3)	5073(2)	24(1)	1
C(20)	6495(3)	8946(2)	4277(2)	18(1)	1
C(21)	7961(4)	10183(3)	4244(2)	37(1)	1
C(22)	5096(3)	10322(2)	2641(2)	16(1)	1
C(23)	5645(3)	11252(2)	2229(2)	17(1)	1
C(24)	4742(3)	12418(3)	2124(2)	23(1)	1
C(25)	3270(3)	12647(3)	2424(2)	26(1)	1
C(26)	2700(3)	11749(3)	2831(2)	24(1)	1
C(27)	3600(3)	10585(3)	2960(2)	19(1)	1
C(28)	1655(3)	9780(3)	3634(2)	30(1)	1
C(29)	4339(3)	8003(3)	2291(2)	21(1)	1
C(30)	10162(3)	7095(3)	2620(2)	20(1)	1
C(31)	9896(3)	6997(3)	3422(2)	29(1)	1
C(32)	10899(3)	6254(3)	3873(2)	33(1)	1
C(33)	12237(3)	5578(3)	3510(2)	29(1)	1
C(34)	12535(3)	5650(3)	2721(2)	24(1)	1
C(35)	11526(3)	6391(2)	2261(2)	18(1)	1
C(36)	11764(3)	6540(2)	1413(2)	19(1)	1
C(37)	13018(3)	5914(3)	959(2)	22(1)	1
C(38)	13125(3)	6110(3)	151(2)	26(1)	1

C(39)	12033(3)	6886(3)	-195(2)	22(1)	1
C(40)	10761(3)	7525(2)	268(2)	20(1)	1
C(41)	10607(3)	7379(2)	1067(2)	15(1)	1
C(51)	9223(11)	4067(8)	3880(6)	32(2)	0.808(2)
Cl(1)	7689(1)	5096(1)	4350(1)	34(1)	0.808(2)
Cl(2)	9251(1)	2575(1)	4336(1)	36(1)	0.808(2)
C(51B)	8800(50)	4220(60)	4050(30)	90(20)	0.192(2)
Cl(1B)	7334(11)	3765(8)	4655(5)	123(4)	0.192(2)
Cl(2B)	10471(12)	3352(9)	4230(6)	137(4)	0.192(2)

Table 14. Selected bond lengths [Å] and angles [°] for 4 (CCDC 208405).

Cr(1)-C(30)	2.035(3)	C(30)-Cr(1)-C(41)	81.95(11)
Cr(1)-C(41)	2.058(3)	C(30)-Cr(1)-O(1)	168.61(9)
Cr(1)-O(1)	2.337(2)	C(41)-Cr(1)-O(1)	89.56(9)
Cr(1)-P(1)	2.4261(8)	C(30)-Cr(1)-P(1)	100.01(8)
Cr(1)-Br(1)	2.4815(5)	C(41)-Cr(1)-P(1)	94.21(7)
Cr(1)-P(2)	2.6608(8)	O(1)-Cr(1)-P(1)	72.94(5)
		C(30)-Cr(1)-Br(1)	93.24(8)
		C(41)-Cr(1)-Br(1)	97.74(7)
		O(1)-Cr(1)-Br(1)	95.43(5)
		P(1)-Cr(1)-Br(1)	163.28(3)
		C(30)-Cr(1)-P(2)	100.21(8)
		C(41)-Cr(1)-P(2)	159.08(8)
		O(1)-Cr(1)-P(2)	85.06(5)
		P(1)-Cr(1)-P(2)	64.89(2)
		Br(1)-Cr(1)-P(2)	102.88(2)

Table 15. Bond lengths [Å] and angles [°] for 4 (CCDC 208405).

Cr(1)-C(30)	2.035(3)	C(17)-C(18)	1.392(4)
Cr(1)-C(41)	2.058(3)	C(17)-H(17)	0.9500
Cr(1)-O(1)	2.3369(19)	C(18)-C(19)	1.383(4)
Cr(1)-P(1)	2.4261(8)	C(18)-H(18)	0.9500
Cr(1)-Br(1)	2.4815(5)	C(19)-C(20)	1.385(4)
Cr(1)-P(2)	2.6608(8)	C(19)-H(19)	0.9500
P(1)-N(1)	1.697(2)	C(21)-H(21A)	0.9800
P(1)-C(1)	1.808(3)	C(21)-H(21B)	0.9800
P(1)-C(8)	1.810(3)	C(21)-H(21C)	0.9800
P(2)-N(1)	1.712(2)	C(22)-C(23)	1.394(4)
P(2)-C(22)	1.820(3)	C(22)-C(27)	1.413(4)
P(2)-C(15)	1.829(3)	C(23)-C(24)	1.388(4)
O(1)-C(6)	1.394(3)	C(23)-H(23)	0.9500
O(1)-C(7)	1.448(3)	C(24)-C(25)	1.388(4)
O(2)-C(13)	1.350(3)	C(24)-H(24)	0.9500
O(2)-C(14)	1.439(3)	C(25)-C(26)	1.370(4)
O(3)-C(20)	1.363(3)	C(25)-H(25)	0.9500
O(3)-C(21)	1.430(3)	C(26)-C(27)	1.389(4)
O(4)-C(27)	1.357(3)	C(26)-H(26)	0.9500
O(4)-C(28)	1.412(3)	C(28)-H(28A)	0.9800
N(1)-C(29)	1.493(3)	C(28)-H(28B)	0.9800
C(1)-C(2)	1.388(4)	C(28)-H(28C)	0.9800
C(1)-C(6)	1.400(4)	C(29)-H(29A)	0.9800
C(2)-C(3)	1.388(4)	C(29)-H(29B)	0.9800
C(2)-H(2)	0.9500	C(29)-H(29C)	0.9800
C(3)-C(4)	1.384(4)	C(30)-C(31)	1.387(4)
C(3)-H(3)	0.9500	C(30)-C(35)	1.425(4)
C(4)-C(5)	1.371(4)	C(31)-C(32)	1.385(4)
C(4)-H(4)	0.9500	C(31)-H(31)	0.9500
C(5)-C(6)	1.390(4)	C(32)-C(33)	1.397(4)
C(5)-H(5)	0.9500	C(32)-H(32)	0.9500
C(7)-H(7A)	0.9800	C(33)-C(34)	1.369(4)
C(7)-H(7B)	0.9800	C(33)-H(33)	0.9500
C(7)-H(7C)	0.9800	C(34)-C(35)	1.398(4)
C(8)-C(9)	1.392(4)	C(34)-H(34)	0.9500
C(8)-C(13)	1.408(4)	C(35)-C(36)	1.464(4)
C(9)-C(10)	1.389(4)	C(36)-C(37)	1.396(4)
C(9)-H(9)	0.9500	C(36)-C(41)	1.419(4)
C(10)-C(11)	1.401(4)	C(37)-C(38)	1.402(4)
C(10)-H(10)	0.9500	C(37)-H(37)	0.9500
C(11)-C(12)	1.368(4)	C(38)-C(39)	1.351(4)
C(11)-H(11)	0.9500	C(38)-H(38)	0.9500
C(12)-C(13)	1.403(4)	C(39)-C(40)	1.418(4)
C(12)-H(12)	0.9500	C(39)-H(39)	0.9500
C(14)-H(14A)	0.9800	C(40)-C(41)	1.387(4)
C(14)-H(14B)	0.9800	C(40)-H(40)	0.9500
C(14)-H(14C)	0.9800	C(51)-Cl(1)	1.777(9)
C(15)-C(16)	1.384(4)	C(51)-Cl(2)	1.793(10)
C(15)-C(20)	1.401(4)	C(51)-H(51A)	0.9900
C(16)-C(17)	1.386(4)	C(51)-H(51B)	0.9900
C(16)-H(16)	0.9500	C(51B)-Cl(2B)	1.70(5)

C(51B)-Cl(1B)	1.77(5)	C(6)-C(5)-H(5)	120.6
C(51B)-H(51C)	0.9900	C(5)-C(6)-O(1)	123.0(2)
C(51B)-H(51D)	0.9900	C(5)-C(6)-C(1)	121.1(2)
		O(1)-C(6)-C(1)	115.9(2)
C(30)-Cr(1)-C(41)	81.95(11)	O(1)-C(7)-H(7A)	109.5
C(30)-Cr(1)-O(1)	168.61(9)	O(1)-C(7)-H(7B)	109.5
C(41)-Cr(1)-O(1)	89.56(9)	H(7A)-C(7)-H(7B)	109.5
C(30)-Cr(1)-P(1)	100.01(8)	O(1)-C(7)-H(7C)	109.5
C(41)-Cr(1)-P(1)	94.21(7)	H(7A)-C(7)-H(7C)	109.5
O(1)-Cr(1)-P(1)	72.94(5)	H(7B)-C(7)-H(7C)	109.5
C(30)-Cr(1)-Br(1)	93.24(8)	C(9)-C(8)-C(13)	118.8(3)
C(41)-Cr(1)-Br(1)	97.74(7)	C(9)-C(8)-P(1)	122.0(2)
O(1)-Cr(1)-Br(1)	95.43(5)	C(13)-C(8)-P(1)	119.0(2)
P(1)-Cr(1)-Br(1)	163.28(3)	C(10)-C(9)-C(8)	120.7(3)
C(30)-Cr(1)-P(2)	100.21(8)	C(10)-C(9)-H(9)	119.6
C(41)-Cr(1)-P(2)	159.08(8)	C(8)-C(9)-H(9)	119.6
O(1)-Cr(1)-P(2)	85.06(5)	C(9)-C(10)-C(11)	119.3(3)
P(1)-Cr(1)-P(2)	64.89(2)	C(9)-C(10)-H(10)	120.3
Br(1)-Cr(1)-P(2)	102.88(2)	C(11)-C(10)-H(10)	120.3
N(1)-P(1)-C(1)	104.37(12)	C(12)-C(11)-C(10)	121.4(3)
N(1)-P(1)-C(8)	105.67(12)	C(12)-C(11)-H(11)	119.3
C(1)-P(1)-C(8)	106.58(13)	C(10)-C(11)-H(11)	119.3
N(1)-P(1)-Cr(1)	97.96(8)	C(11)-C(12)-C(13)	119.1(3)
C(1)-P(1)-Cr(1)	104.71(9)	C(11)-C(12)-H(12)	120.4
C(8)-P(1)-Cr(1)	134.14(9)	C(13)-C(12)-H(12)	120.4
N(1)-P(2)-C(22)	108.23(12)	O(2)-C(13)-C(12)	124.9(3)
N(1)-P(2)-C(15)	106.44(12)	O(2)-C(13)-C(8)	114.4(2)
C(22)-P(2)-C(15)	101.96(12)	C(12)-C(13)-C(8)	120.6(3)
N(1)-P(2)-Cr(1)	89.33(8)	O(2)-C(14)-H(14A)	109.5
C(22)-P(2)-Cr(1)	121.14(9)	O(2)-C(14)-H(14B)	109.5
C(15)-P(2)-Cr(1)	126.73(9)	H(14A)-C(14)-H(14B)	109.5
C(6)-O(1)-C(7)	115.2(2)	O(2)-C(14)-H(14C)	109.5
C(6)-O(1)-Cr(1)	121.70(15)	H(14A)-C(14)-H(14C)	109.5
C(7)-O(1)-Cr(1)	119.23(15)	H(14B)-C(14)-H(14C)	109.5
C(13)-O(2)-C(14)	117.1(2)	C(16)-C(15)-C(20)	118.7(3)
C(20)-O(3)-C(21)	116.8(2)	C(16)-C(15)-P(2)	124.5(2)
C(27)-O(4)-C(28)	119.8(2)	C(20)-C(15)-P(2)	116.8(2)
C(29)-N(1)-P(1)	121.55(18)	C(15)-C(16)-C(17)	120.5(3)
C(29)-N(1)-P(2)	128.34(18)	C(15)-C(16)-H(16)	119.7
P(1)-N(1)-P(2)	106.76(12)	C(17)-C(16)-H(16)	119.7
C(2)-C(1)-C(6)	118.5(3)	C(16)-C(17)-C(18)	119.8(3)
C(2)-C(1)-P(1)	125.3(2)	C(16)-C(17)-H(17)	120.1
C(6)-C(1)-P(1)	116.2(2)	C(18)-C(17)-H(17)	120.1
C(3)-C(2)-C(1)	120.6(3)	C(19)-C(18)-C(17)	120.8(3)
C(3)-C(2)-H(2)	119.7	C(19)-C(18)-H(18)	119.6
C(1)-C(2)-H(2)	119.7	C(17)-C(18)-H(18)	119.6
C(4)-C(3)-C(2)	119.4(3)	C(18)-C(19)-C(20)	118.8(3)
C(4)-C(3)-H(3)	120.3	C(18)-C(19)-H(19)	120.6
C(2)-C(3)-H(3)	120.3	C(20)-C(19)-H(19)	120.6
C(5)-C(4)-C(3)	121.5(3)	O(3)-C(20)-C(19)	124.5(3)
C(5)-C(4)-H(4)	119.2	O(3)-C(20)-C(15)	114.1(2)
C(3)-C(4)-H(4)	119.2	C(19)-C(20)-C(15)	121.4(3)
C(4)-C(5)-C(6)	118.8(3)	O(3)-C(21)-H(21A)	109.5
C(4)-C(5)-H(5)	120.6	O(3)-C(21)-H(21B)	109.5

H(21A)-C(21)-H(21B)	109.5	C(31)-C(32)-H(32)	120.5
O(3)-C(21)-H(21C)	109.5	C(33)-C(32)-H(32)	120.5
H(21A)-C(21)-H(21C)	109.5	C(34)-C(33)-C(32)	120.0(3)
H(21B)-C(21)-H(21C)	109.5	C(34)-C(33)-H(33)	120.0
C(23)-C(22)-C(27)	118.8(3)	C(32)-C(33)-H(33)	120.0
C(23)-C(22)-P(2)	118.0(2)	C(33)-C(34)-C(35)	121.4(3)
C(27)-C(22)-P(2)	123.2(2)	C(33)-C(34)-H(34)	119.3
C(24)-C(23)-C(22)	120.9(3)	C(35)-C(34)-H(34)	119.3
C(24)-C(23)-H(23)	119.5	C(34)-C(35)-C(30)	119.3(3)
C(22)-C(23)-H(23)	119.5	C(34)-C(35)-C(36)	125.1(3)
C(23)-C(24)-C(25)	119.1(3)	C(30)-C(35)-C(36)	115.5(2)
C(23)-C(24)-H(24)	120.4	C(37)-C(36)-C(41)	120.8(3)
C(25)-C(24)-H(24)	120.4	C(37)-C(36)-C(35)	124.0(3)
C(26)-C(25)-C(24)	121.2(3)	C(41)-C(36)-C(35)	115.2(2)
C(26)-C(25)-H(25)	119.4	C(36)-C(37)-C(38)	119.4(3)
C(24)-C(25)-H(25)	119.4	C(36)-C(37)-H(37)	120.3
C(25)-C(26)-C(27)	120.2(3)	C(38)-C(37)-H(37)	120.3
C(25)-C(26)-H(26)	119.9	C(39)-C(38)-C(37)	121.2(3)
C(27)-C(26)-H(26)	119.9	C(39)-C(38)-H(38)	119.4
O(4)-C(27)-C(26)	124.5(3)	C(37)-C(38)-H(38)	119.4
O(4)-C(27)-C(22)	115.8(2)	C(38)-C(39)-C(40)	119.3(3)
C(26)-C(27)-C(22)	119.7(3)	C(38)-C(39)-H(39)	120.3
O(4)-C(28)-H(28A)	109.5	C(40)-C(39)-H(39)	120.3
O(4)-C(28)-H(28B)	109.5	C(41)-C(40)-C(39)	121.8(3)
H(28A)-C(28)-H(28B)	109.5	C(41)-C(40)-H(40)	119.1
O(4)-C(28)-H(28C)	109.5	C(39)-C(40)-H(40)	119.1
H(28A)-C(28)-H(28C)	109.5	C(40)-C(41)-C(36)	117.5(3)
H(28B)-C(28)-H(28C)	109.5	C(40)-C(41)-Cr(1)	129.2(2)
N(1)-C(29)-H(29A)	109.5	C(36)-C(41)-Cr(1)	113.3(2)
N(1)-C(29)-H(29B)	109.5	Cl(1)-C(51)-Cl(2)	109.1(5)
H(29A)-C(29)-H(29B)	109.5	Cl(1)-C(51)-H(51A)	109.9
N(1)-C(29)-H(29C)	109.5	Cl(2)-C(51)-H(51A)	109.9
H(29A)-C(29)-H(29C)	109.5	Cl(1)-C(51)-H(51B)	109.9
H(29B)-C(29)-H(29C)	109.5	Cl(2)-C(51)-H(51B)	109.9
C(31)-C(30)-C(35)	117.6(3)	H(51A)-C(51)-H(51B)	108.3
C(31)-C(30)-Cr(1)	128.5(2)	Cl(2B)-C(51B)-Cl(1B)	115(4)
C(35)-C(30)-Cr(1)	113.6(2)	Cl(2B)-C(51B)-H(51C)	108.6
C(32)-C(31)-C(30)	122.6(3)	Cl(1B)-C(51B)-H(51C)	108.6
C(32)-C(31)-H(31)	118.7	Cl(2B)-C(51B)-H(51D)	108.6
C(30)-C(31)-H(31)	118.7	Cl(1B)-C(51B)-H(51D)	108.6
C(31)-C(32)-C(33)	119.0(3)	H(51C)-C(51B)-H(51D)	107.6

Table 16. Anisotropic displacement parameters ($Å^2 x 10^4$) for 4 (CCDC 208405). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr(1)	114(2)	142(3)	196(3)	-37(2)	-45(2)	-11(2)
Br(1)	193(2)	196(2)	298(2)	-52(1)	-83(1)	-61(1)
P(1)	143(4)	131(4)	159(4)	-28(3)	-22(3)	-28(3)
P(2)	158(4)	133(4)	157(4)	-28(3)	-22(3)	-29(3)
O(1)	139(10)	106(10)	224(11)	-14(8)	-65(8)	-44(8)
O(2)	168(10)	164(11)	286(12)	-53(9)	20(9)	-19(9)
O(3)	249(11)	300(12)	227(12)	-23(10)	-69(9)	-148(10)
O(4)	169(11)	231(12)	322(13)	-48(10)	63(9)	-57(9)
N(1)	122(12)	169(13)	188(13)	-65(10)	-8(10)	-28(10)
C(1)	84(13)	139(15)	173(16)	-26(12)	-18(12)	9(11)
C(2)	158(14)	168(16)	224(17)	-46(13)	-25(13)	-60(12)
C(3)	156(15)	214(17)	209(17)	-66(14)	-54(13)	-45(13)
C(4)	126(14)	262(17)	184(16)	-44(14)	-53(12)	6(13)
C(5)	112(14)	134(15)	232(17)	-17(13)	-9(12)	-17(12)
C(6)	57(13)	157(15)	170(16)	-53(12)	-17(11)	7(11)
C(7)	186(15)	144(16)	227(17)	35(13)	-35(13)	-67(13)
C(8)	208(15)	172(16)	174(16)	-43(13)	-63(13)	-61(13)
C(9)	241(16)	195(17)	241(18)	-31(14)	-90(14)	-77(13)
C(10)	295(18)	261(18)	194(17)	41(14)	-54(14)	-143(15)
C(11)	393(19)	167(17)	239(18)	34(14)	-151(15)	-117(15)
C(12)	256(17)	161(16)	278(19)	-70(14)	-99(14)	-35(13)
C(13)	219(16)	205(17)	174(16)	-6(13)	-62(13)	-95(13)
C(14)	169(15)	192(17)	380(20)	-88(15)	-18(14)	1(13)
C(15)	208(15)	159(16)	162(16)	-33(13)	-20(13)	-20(13)
C(16)	540(20)	310(20)	205(19)	-26(15)	-49(17)	-213(17)
C(17)	600(20)	370(20)	290(20)	15(17)	-28(18)	-286(19)
C(18)	600(20)	380(20)	164(18)	1(16)	-55(17)	-216(19)
C(19)	278(17)	258(18)	198(18)	-54(14)	-41(14)	-72(14)
C(20)	136(14)	152(16)	208(17)	-30(13)	-15(12)	1(12)
C(21)	400(20)	530(20)	330(20)	18(18)	-149(17)	-326(19)
C(22)	174(15)	162(16)	142(16)	-42(12)	-19(12)	-26(12)
C(23)	163(14)	183(16)	189(16)	-34(13)	-69(12)	-50(12)
C(24)	313(18)	153(16)	251(18)	-32(14)	-75(14)	-75(14)
C(25)	246(17)	165(17)	340(20)	-85(15)	-123(15)	48(14)
C(26)	150(15)	276(19)	271(18)	-107(15)	-40(13)	-3(14)
C(27)	199(15)	202(17)	173(16)	-69(13)	-21(13)	-36(13)
C(28)	184(16)	430(20)	286(19)	-133(16)	62(14)	-131(15)
C(29)	139(15)	235(17)	288(18)	-89(14)	-17(13)	-66(13)
C(30)	171(15)	208(17)	237(17)	-57(14)	-70(13)	-25(13)
C(31)	231(17)	300(19)	270(19)	-58(15)	-86(14)	48(14)
C(32)	317(19)	350(20)	261(19)	-53(16)	-119(15)	21(16)
C(33)	280(18)	233(18)	330(20)	26(15)	-182(15)	-18(14)
C(34)	172(15)	157(16)	380(20)	-65(14)	-82(14)	-3(13)
C(35)	135(14)	133(15)	283(18)	-36(13)	-68(13)	-34(12)
C(36)	129(14)	178(16)	287(18)	-59(14)	-40(13)	-69(12)
C(37)	116(14)	180(17)	360(20)	-91(14)	3(14)	-27(12)
C(38)	133(15)	199(17)	420(20)	-146(15)	97(14)	-50(13)

C(39)	236(16)	239(17)	201(17)	-51(14)	13(13)	-132(14)
C(40)	148(15)	171(16)	293(19)	-43(14)	-46(13)	-50(12)
C(41)	125(14)	130(15)	221(17)	-26(12)	-38(12)	-63(12)
C(51)	370(50)	260(30)	310(40)	-70(30)	-110(30)	-10(30)
Cl(1)	380(6)	263(6)	316(6)	-87(5)	-134(5)	42(5)
Cl(2)	402(6)	232(6)	424(7)	-105(5)	-71(5)	-16(5)
C(51B)	700(400)	1500(500)	900(400)	-100(300)	-100(300)	-700(400)
Cl(1B)	1570(80)	1140(70)	1260(80)	-90(60)	-680(70)	-540(60)
Cl(2B)	1480(90)	1250(80)	1110(70)	-510(60)	320(70)	-200(70)

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